DOCTOR OF PHILOSOPHY

Ternary combination concretes using GGBS, fly ash & limestone strength, permeation & durability properties

Buss, Kirsty

Award date:
2012

DOCTOR OF PHILOSOPHY

Ternary combination concretes using GGBS, fly ash & limestone

strength, permeation & durability properties

Kirsty Buss

2013

University of Dundee

TERNARY COMBINATION CONCRETES USING GGBS, FLY ASH & LIMESTONE: STRENGTH, PERMEATION & DURABILITY PROPERTIES

by

KIRSTY BUSS

BSC (HONS), MRES

A thesis presented in application for the
Degree of Doctor of Philosophy
Department of Civil Engineering
University of Dundee
August2012

DECLARATION

I hereby declare that I am the author of this thesis and that the work recorded has been composed by me, and that all references citied have been consulted, and that it has not been previously used for a higher degree**.**

Kirsty I Buss

CERTIFICATE

This is to certify that Kirsty I Buss has completed research under my supervision, and that she has fulfilled the conditions of the relevant Ordinances and Regulations of the University of Dundee, so that she is qualified to submit this thesis in application for the Degree of Doctor of Philosophy.

Dr M J McCarthy

Department of Engineering

University of Dundee

ACKNOWLEDGEMENTS

This dissertation would not have been possible without the guidance and the help of several individuals who in one way or another contributed and extended their valuable assistance in the preparation and completion of this study. Foremost I wish to take this opportunity to express my sincere gratitude to Dr Michael McCarthy for his continued support and guidance throughout this journey. His knowledge and expertise has been an invaluable asset to my studies.

I extend my thanks to both the academic and technical staff of the School of Civil Engineering for their continued assistance amongst these specifically I wish to thank Dr Li Zheng and Dr Judith Halliday for their advice during the early stages of my study and Dr Murray Newlands for his support and encouragement during the latter. The industrial partners, namely, Aggregate Industries UK Ltd, Castle Cement Ltd, Cementitious Slag Makers Association, Imerys, John Doyle Group, Mineral Products Association and Omya UK Ltd are also gratefully acknowledge for their funding of the project.

Most importantly I wish to express my most sincere gratitude for the support and patience of family and friends. To the best Aunt and Uncle who have stood in as proud and supportive parents, together with Angela and Martin. Thanks to Linda and Andrew for their tireless proof-reading and encouragement. Thanks also to Ann and Lesley, for your patience and friendship, and Linda for keeping my mind, body and soul intact. Also to the many who have kept me company and sane along this journey; David, Maziah and Sadi especially.

I wish to dedicate this work to three amazing women. To my mother, who gave me gift of life and perseverance and to my friend Maureen, whose faith and confidence in my abilities surpassed all others and whose encouragement kept me on the right path when my own steps faltered. Finally, and by no means least, to Mandy, my eldest sister whose own strength and determination is something to be admired and aspired to by all, a true Paralympian.

ABSTRACT

With the pressure on the construction industry to lower CO_2 emissions it has become increasingly important to utilise materials that supplement Portland cement (CEM I) in concrete. These include additions such as ground granulated blast-furnace slag (GGBS) and fly ash, which have found greater use due to the benefits they provide to many properties of the material (in addition to environmental impact). While studies have investigated these materials in binary blends with CEM I, little work has examined the effect of combining materials in ternary blend concretes. A wide-ranging study was, therefore, set up to examine this for the range of more commonly available additions. This thesis reports on research carried out to investigate the effects of cement combinations based on CEM I / GGBS with either fly ash or limestone. The experimental programme investigated these materials in both paste and concrete and covered fresh properties, compressive strength, permeation and durability properties (using standard water curing for the latter three) and considered, for the hardened properties, how these may be balanced with environmental cost.

The mixes covered a range of w/c ratios (0.35. 0.50 and 0.65), which was the main basis of comparison, and combinations of CEM I with GGBS (at levels of 35%, 55% and 75%), and fly ash and LS part-replacing this (at levels of 10 to 20 % and 10 to 35% respectively), after consideration of the relevant standards and related research. The initial phase of the study examined the characteristics of the materials, which indicated that they conformed to appropriate standards and were typical of those used in the application. Studies with cement paste (0.35 and 0.50 w/c ratio) indicated that there were reductions in water demand with the use of addition materials (binary and ternary) compared to CEM I. The setting times of the cement pastes were also affected, generally increasing with GGBS level for the binary mixes, although the effect was influenced by w/c ratio. Whilst fly ash and limestone delayed setting at the higher w/c ratio, the opposite occurred as this reduced, compared to the binary mixes. It was also found that the yield stress increased with GGBS level and further with the addition of ternary materials (particularly limestone) compared to CEM I.

The superplastiser (SP) dosage requirement in concrete was found to decrease with increasing w/c ratio, and ternary additions reduced this compared to binary and CEM I concrete with the effect most noticeable at low w/c ratio. Early strength development was less than CEM I for binary concretes and differences increased with GGBS level. Improvements with the introduction of fly ash compared to the binary concretes were noted with increasing GGBS levels and w/c ratio. In general, the addition of LS gave reduced early strength for all concretes. Although at the 35% GGBS level binary concretes achieved similar strength to those of CEM I, the others generally gave reductions at all ages to 180 days, with differences increasing with GGBS level. However, with increasing w/c ratio and GGBS level improved strength development of ternary concretes, was noted compared to those of CEM I from 28 days.

Permeation (absorption (initial surface absorption and sorptivity) and permeability (water penetration and air permeability)) and durability properties (accelerated carbonation and chloride ingress) of the test concrete were also investigated. At 28 days, for low GGBS levels, the binary concretes gave reduced absorption properties compared to CEM I, while the reverse occurred at high level. The effect of the ternary concretes gave further improvements at the lower GGBS levels and with increasing w/c ratio and curing time compared to CEM I. At the higher GGBS level the effect of the ternary additions was less noticeable but, in the case of limestone, improvements were still seen with increasing w/c ratio compared to CEM I. Similar effects were noted for the sorptivity results. The air permeability results gave higher values at 28 days for the binary and ternary concretes compared to CEM I, but significant improvements in the long-term at the lower GGBS level across the range of w/c ratios compared to CEM I concrete. Similar trends were found with water penetration tests. Accelerated carbonation increased with GGBS level for binary concretes compared to CEM I. These differences increased further with the introduction of fly ash and LS, particularly the former. In contrast rapid chloride tests indicated improvements with increasing GGBS levels compared to CEM I and further benefits with the inclusion of fly ash and limestone.

Embodied CO_2 (ECO_2) was calculated based on published British Cement Association (BCA) values for each component of the mix and was shown to reduce with increasing w/c ratio and addition level in concrete. For concrete of an equal strength of 40N/mm^2 the ECO_2 could be almost halved (reduced from 343 kg/m^3 for the CEM I to 176 kg/m^3) for the ternary concretes at higher GGBS levels. These combination concretes also gave enhanced durability with regard to chloride ingress and at the lower w/c ratio comparable properties to CEM I in the case of carbonation. Overall, the results suggest that there is potential for ternary concretes to be used in the concrete industry given their ability to reduce ECO_2, without compromising strength, permeation and durability properties of concrete.

Contents

LIST OF FIGURES & TABLES

CHAPTER ONE: INTRODUCTION

1.1 Background

Due to growing environmental concerns over resource use and global warming, there is increasing pressure on the construction industry to reduce the environmental impact of cement and concrete production. Acquisition of primary aggregates and CO_2 emissions from production are considered unacceptable, yet the growth of infrastructure, cities and society as a whole has deemed it necessary to supply concrete to achieve these. Ramachandran et al described concrete as "the largest production of all man-made materials" (*2001*). Neville noted that together with steel it is the "most commonly used structural material" (*1995*). Figures from CEMBUREAU indicate that 2009 production of cement reached over 3 billion tonnes globally (*CEMBUREAU, 2009)*. These figures belie the humble beginnings of cement that date back millennia. Ancient Egyptians, Greeks and Romans all used the material, with the Roman term "*opus caementicium*" being the first instance of the use of the word cement by Vetruvius in his treatise "*Ten Books on Architecture"* first published in 25BC (*Vetruvius, 2008*). As a material it may well have been used continuously, but there are little records of this until the technical knowledge of its manufacture began to develop in the 18th century. James Parker patented "Roman cement" in 1796 beginning an influx of developing cements by the likes of John Smeaton, Louis Vicat, James Frost and Joseph Aspdin in 1824 with Portland cement (*Francis, 1977*). However it was the 1840's that saw the production of modern Portland cement, thus beginning a growth of concrete use in the construction industry to what has now become a multi-billion pound global industry which now has far reaching consequences in terms of the environment, economy and society as a whole.

1.1.1 Impact of Concrete on Modern Society

In a modern society, despite its continued and extensive use, concrete brings pressures to the industry in an ever growing global market that is encouraged to work towards more sustainable development. The impact of cement production is threefold affecting the pillars of

sustainable development: environment, economic and social in four fundamental areas which are summarised in Table 1.1 below.

Table 1.1: Impact of the cement industry *(summarised from The Concrete Society, 2009)*

Environmental Impact	Social Impact	Economic Impact
Land use and natural resource management.	Recreation v Industry	Transportation costs (local v imported)
Waste to landfill	Landfill sites	Taxes
Working environment	Health and safety	Costs incurred due to sickness. Medical bills
Emissions and energy	Reduction commitment	Energy taxes

Natural resources are used throughout the manufacture of cement and further still for concrete, with the continued acquisition of aggregates; these can leave obvious scars in the environment due to quarrying processes. Over time, these can be removed with re-integration of quarries into the landscape, allowing them to be re-cultivated or returned to nature *(The Concrete Society, 2009)*. Quarrying can also incur added costs as material requires to be transported to processing sites. Locally sourced materials can reduce costs and the use of recycled materials, including crushed concrete and brick, are also encouraged. Not only does this reduce natural resource use, it reduces material entering the waste stream. This in turn decreases waste from the construction industry going to landfill, reducing associated taxes.

The reduction in the economic impact of concrete with respect to these can be twofold, reducing taxes and lowering production and transportation costs, especially if processing can be done on site. Social impact from industry also occurs with working environments within construction being hazardous. Furthermore, the cement industry itself has certain risks with wet cement causing skin burns due to its being caustic, whilst the dry powder can cause severe respiratory irritation (*HSE, 2002*). Automated production within processing plants can reduce this impact but creates additional costs and replaces the workforce, increasing unemployment. Additional health issues can be associated with heavy metals present in the clinker and emissions during cement production (*HSE, 2002*). These will depend on the composition of the raw materials used but gases and dust rich in volatile heavy

metals are released into the atmosphere during the high temperature calcination process of the limestone and clay minerals. In European countries this is regulated but in the developing world it is still very much a concern and lends support to the argument for the use of alternative materials to Portland cement in concrete construction (*McLeod, 2005*).

1.1.2 Climate Change

Whilst these issues are important, it is the significant emissions of CO_2 that are of the greatest importance on a global scale. By making improvements in this area, the other impacts can also be reduced (*McLeod, 2005*). Damineli et al (*2010*) reported that 5.0% of anthropogenic CO_2 emissions were caused by cement production in 2003 and this is set to increase twofold by 2050, with the majority occurring in developing countries. Given the quantities shown in Figure 1.1, which illustrates cement production by region and country on a global scale, it is clear that developing countries such as China, Africa and India are increasing their cement production compared to those in Europe. This is made all the more evident in Figure 1.2 that shows the evolution of cement production from 2000 to 2010, production in Africa and Asia has risen steadily during this timeframe to indicate an increase of 125% and 145%, respectively, on 2000 data. It must be noted that these figures are based on cement production as a whole and it is not indicated by CEMBUREAU what percentage of these figures are specifically Portland cement production. Regardless, however, it stresses the fact that this is an international issue and has given rise, over the past few decades, to policies, strategies and agreements on reducing CO_2 emissions towards encouraging sustainable development. Such policies include the Kyoto Protocol (1997) and subsequent agreements between governments to reduce their CO_2 emissions that have been transferred down the various levels of governance to local authorities by way of planning strategies and industry commitments towards more sustainable development. Across the CEMBUREAU countries production rates have changed. Figure 1.3 indicates the percentage difference in production in each member country when 2010 data is compared to 2009. Whilst there are percentage changes it is not until the *Per Capita* consumption of 2010 is examined in Figure 1.4 that the true production of cement can be realised.

BCA (*2008*) indicate that for every tonne of cement produced 930kg of CO_2 is emitted, that is 93% of the manufactured volume. It is widely recognised that this needs to be reduced

and the concrete industry on the whole, is making headway. The ability to reduce the production of cement, and hence environmental impact, but still meet the demands of industry by supplying a durable and strong material has led to a great deal of research into the use of pozzolana, that are capable of providing durable concrete. Both natural pozzolana in the form of pumice, and artificial pozzolana such as pottery were used by the Romans to great success (*Sisomondo, 2009*). The extensive Roman aqueducts used pozzolanic cements and the monolithic dome of the Pantheon in Rome and the Baths of Caracella remain standing as a testament to the strength and durability of the materials and the ingenuity of the engineers of that time (*Hill, 1984*).

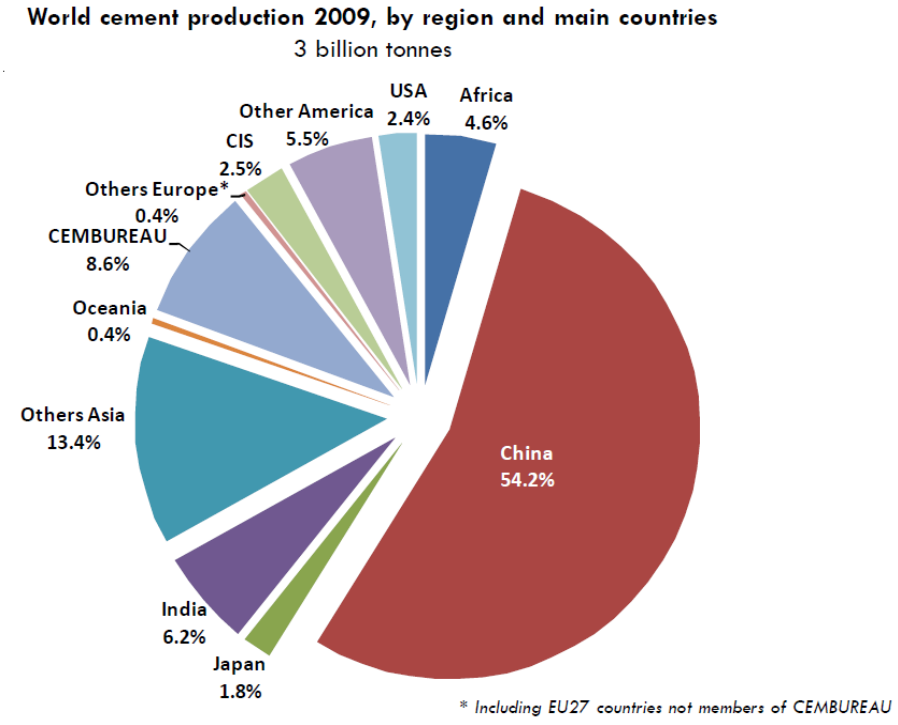


Fig 1.1: Global cement production in 2009

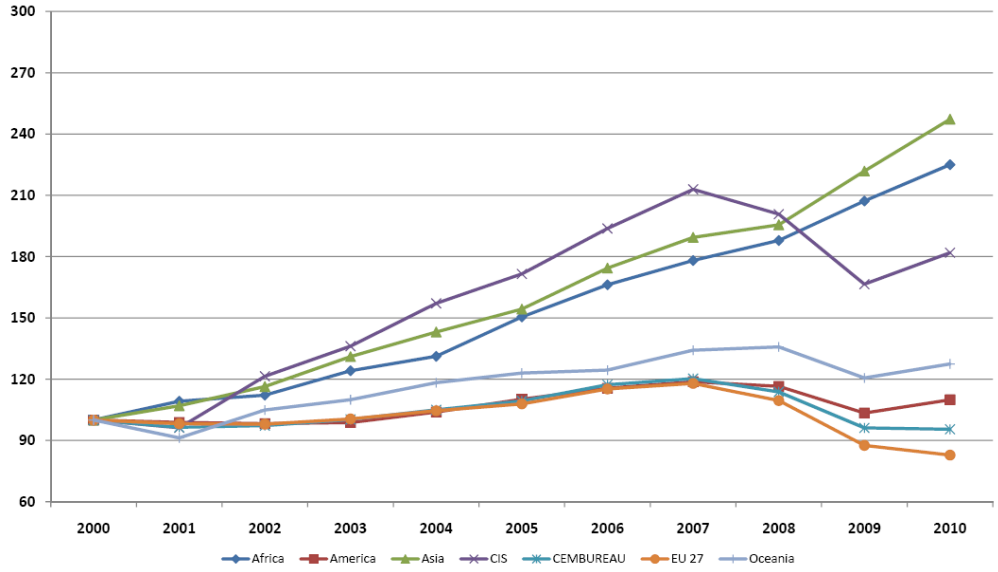
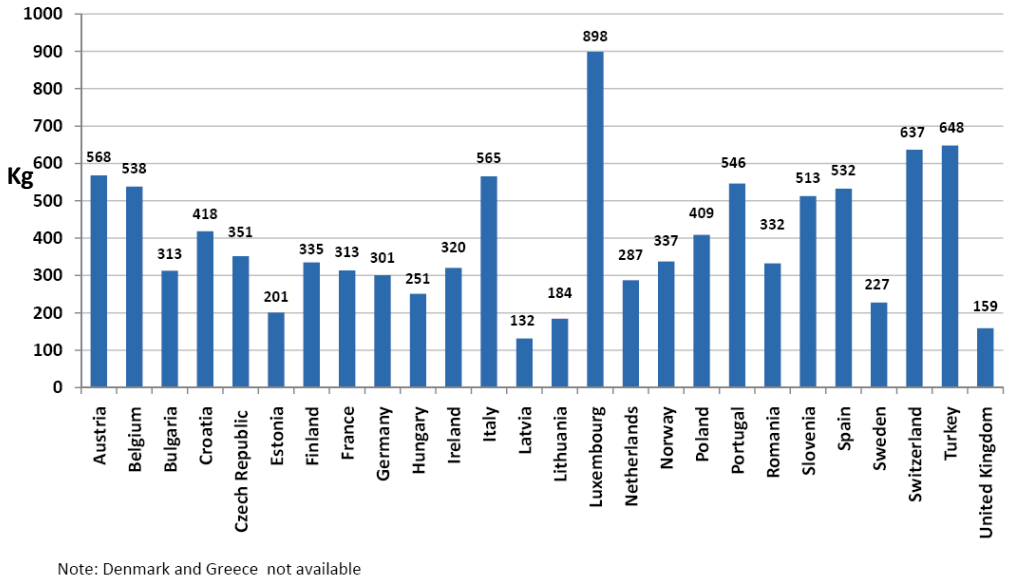


Fig 1.2: Evolution of cement production from 2000 to 2010

Fig 1.3: Cement production across CEMBUREAU countries, 2010 figures compared to 2009



Note: Denmark and Greece not available

Fig 1.4: Per capita cement consumption across CEMBUREAU countries 2010 (Kg)

Recent developments in concrete construction, particularly BS EN 197, mean that there is now a greater range of materials (cements and admixtures) and options than have traditionally been available to engineers to satisfy the needs of the industry as a whole, including environmental. However, the concrete must continue to meet specific technical serviceability requirements that relate to both its engineering and durability properties, as well as achieving all these at a minimum cost. Globally there are differences in terminology for additional materials such as GGBS and fly ash, in cement. Whilst some may refer to them as admixtures this can lead to confusion, as this term usually refers to super-plasticisers, retarding liquids etc., that are added during the mixing process to achieve a certain purpose. Additions seems to be the most accepted term and henceforth will be used throughout this thesis to include GGBS, fly ash and limestone that are added to the Portland cement to produce binary and ternary combination concretes.

1.1.3 Recent Practical Applications of Combination Concretes

On a global scale the use of additions, combined with Portland cement is becoming more common. A number of structures have been made using GGBS as a binary material. In New Zealand a 65% GGBS binary mix was used for the Meridian Energy building in Wellington (*www.sustainableconcrete.org.nz, 2010)*. In the USA, the use of GGBS is state-wide with a federal building in San Francisco (*PCA, 2010*), The Helena (*PCA, 2010*) in New York (using 45%

GGBS) and a 40% GGBS binary mix being used for a new Eco Office in Atlanta (*PCA, 2010*). An elementary school in Hanover, Pennsylvania opened in 2003 (*PCA, 2010*). The structure utilised a 60% GGBS binary mix to produce insulating concrete forms. In the UK the use of GGBS as an addition at a level of 90% with Portland cement has been adopted. Due to its low heat properties and its low strength gain this was used in the cement grout for the encapsulation process, in the decommissioning of Sellafield nuclear power plant (*Hanson, 2010*). Other examples of GGBS being used as a binary addition include the QE2 Bridge on the M25 at Dartford and the construction of the Channel Tunnel rail link, both adopting 70% GGBS to protect steel reinforcement by minimising the ingress of Chloride from de-icing salts (*Hanson, 2010*). A blend of 50% GGBS was used for sea defences at Blackpool beach for their durability and environmental benefits (*Hanson, 2010*).

The use of ternary blended concretes are less widely reported, yet were recognised in Australia as early as 1966 by Specified Concrete Pty Ltd in Wollongong, NSW (*Hinczak & Roper, 1990: Hinczak et al, 1992*) and accepted for industrial use in 1967. In more recent years, ternary mixes have been used for a number of large civil engineering projects. In Honk Kong the Tsa Ma Bridge, spanning nearly 2200m, utilised GGBS and silica fume, as well as fly ash and silica fume ternary blends, as they gave lowest chloride penetration values when tested in the laboratory (*Elkem, 2001*). Fly ash and silica fume have been used as ternary blends in other high profile structures including the Burj Dubai (*Baker, 2007*), the Pacific First Centre, USA (*Shah, 1994*) and the Petronas Twin Towers, Malaysia (*Rivera-Villarreal, 1997*). Construction of the Reliant NFL Stadium in Houston, Texas, completed in 2002 used a ternary mix of 50% CEM I + 30% GGBS + 20% fly ash.

The adoption of both GGBS and fly ash, with their many noted benefits has increased globally due to pressures placed on the industry. 1996 figures produced by Detweiler et al (*1996*) stated that in the UK production of GGBS was in the region of 4 million tonnes with 100% of it being used by the construction industry, reducing CO_2 emissions and waste going to landfill. Current figures from the Cementitious Slag Makers Association (CSMA) indicate this quantity has considerably reduced to 1.5 million tonnes (*Higgins, 2011*) with 100% still being used in concrete. This decline, undoubtedly due to the recession and lower production rates, clearly implies a limited supply of a useful material. By creating ternary blended concretes by

using additional materials such as fly ash and limestone, the benefits of GGBS concretes can be produced and potentially enhanced, whilst extending the availability.

Fly ash utilisation has not risen since 1997 by proportion. 6.2 million tonnes were produced (*UKQAA, 2002*) of which 2.8% was utilised in blended cements and 8% as concrete additions. Figure 1.5 shows that in 2009 the percentage used in different applications has changed very little, with a slight increase to 11% for cement additions (*UKQAA, 2010*). The UKQAA also indicate that production of fly ash in 2010 had reduced to 4.59 million tonnes in the UK (*Sear, 2011*). ECOBA published production figures for all coal combustions products (CCPS) in 2008 as 56 million tonnes across 15 European countries (*ECOBA, 2011*), of which 66% was fly ash.

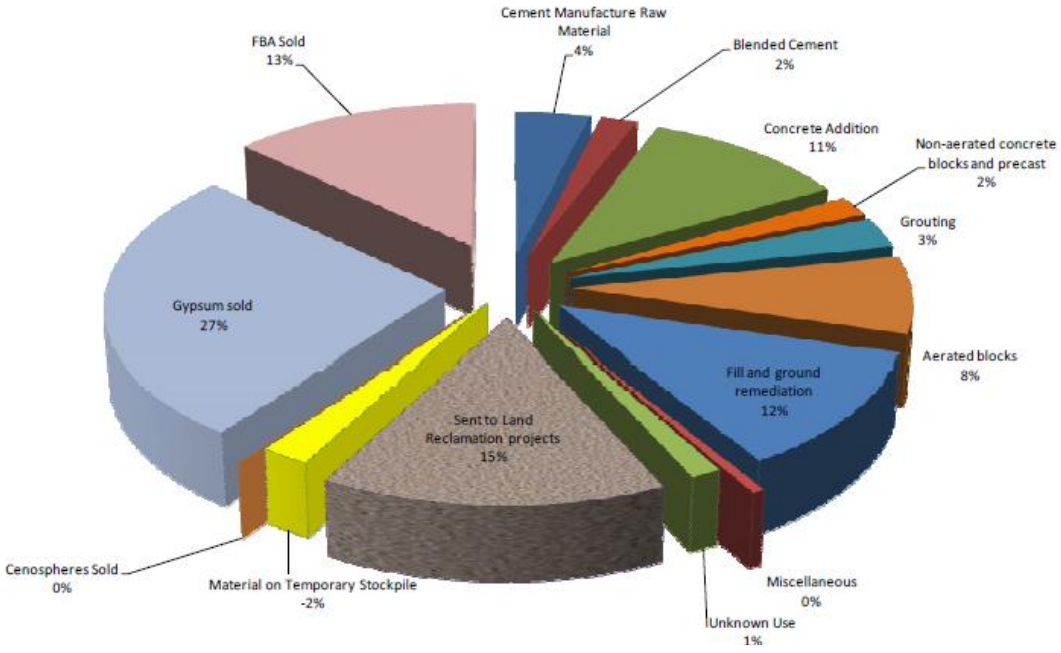


Fig 1.5: Coal Fired Power Station Products Sold During 2009, (UKQAA, 2010)

It has become more apparent, due to increasing awareness, of the need to embrace the main principles of sustainability in concrete technology and the construction industry as a whole. Specific areas requiring attention include materials, waste, energy and pollution. In terms of practical implementation of sustainable development and policy the concrete industry prides itself on being one of the leaders but further development in the way materials are

produced and used, including their life-cycle, remains essential for further progress in this area (*Concrete Society, 2009*). Therefore, there is a clear need to establish what can be achieved with the wider range of materials available in order that they can be fully exploited from both technical and commercial points of view, while at the same time establishing procedures that promote sustainability.

Combining materials such as GGBS and fly ash with cement not only has the potential for reducing the environmental impact of cement but reduces water requirements for equal workability and brings additional benefits such as increasing strength and durability. Progress has been made in this area with the development of new European cement and concrete standards (BS EN 197-1, BS EN 206-1 and BS EN 151671-1) which provide a framework for engineers to appropriately use the materials for a given set of conditions. These are however, conservative out of necessity and are limited in the extent that they permit the use and combination of these materials that are arguably being underexploited. Furthermore, while some work has attempted to examine different cement combinations and they have been used in a few projects, this has been to a very limited extent. To date, research has investigated specific properties such as strength, permeation or durability but as yet there has not been a holistic approach to examining the properties of ternary combinations with regard to the effects that they may bring to concrete. It is therefore the purpose of this study to investigate the behaviour of cement combinations and their influences on (i) the physical properties of the cement paste phase (ii) specific issues associated with concrete performance and (iii) how these may be balanced with environmental impact. As part of a wide-ranging study the focus of this research was on the effects of cement combinations based on CEM I/GGBS with fly ash or limestone replacing GGBS by mass, to give ternary combinations. Blended concretes generally refer to those whose dry materials are blended prior to mixing. This study uses binary and ternary materials that are combined together during the mixing process and will be referred to as combined, or combination, concretes for the purpose of this thesis.

1.2 Aims & Objectives

The aim of the research project was to determine the effects of cement combinations on the macro- and micro- structural properties of the cement paste phase and their influence on aspects of concrete performance.

To meet this aim, a series of specific objectives were established as follows:

1. Physically and chemically characterise the range of materials to be used. Thereafter formulate cement combinations and examine their impact on water demand, SP dosage and rheology characteristics of cement paste.
2. Determine the fresh and early properties of concrete combinations and the effects of cement additions on admixture demand.
3. Investigate the impact of cement combinations on the cement paste structure, using selected methods identified from the literature review.
4. Identify cement combinations giving optimum characteristics with cement paste and examine their impact on the permeation characteristics including the microstructure (low, medium and high w/c ratio) in concretes.
5. Test the concretes to determine an optimum combination with respect to aspects of durability. Specifically examining the concretes in terms of their resistance to both carbonation and chloride ingress, thus establishing the benefits and limitations of using combined materials to produce ternary mixes.
6. Examine the cement combination concretes with regard to their influence on ECO_2 and consider balancing sustainability and aspects of concrete performance.

1.3 Scope of the Study

The use of additions has been a well-researched topic for many years and the benefits of the materials used in this study as binary additions are well established. It is widely recognised that GGBS and fly ash both increase strength over time, it can also give enhanced permeation properties. However, it is also known that these materials have slow early strength development and poor resistance to carbonation, thus restricting their use in some circumstances. Whilst there is a basic understanding of the effects of these materials individually in binary concretes, limited knowledge exists as to the effects of combining GGBS with fly ash or limestone to create ternary concretes.

Combining materials such as these will create different effects within the cement paste phase that influences the properties, compared to those of binary concretes. With the addition of fly ash, competition between this and GGBS, for free lime within concrete may influence

strength development and other properties. The inclusion of limestone, considered to be an inert filler, may improve early strength as a denser microstructure is produced or it may act as a catalyst for the hydration of GGBS. Bearing this in mind, a number of ternary concretes were established to examine these effects and their influence on properties such as strength and durability. Specifically of interest was whether the addition of a ternary material would improve the early strength development of the concretes tested and also give improved resistance to carbonation.

Initially a number of standard material characterisation tests, to contribute to the understanding of how these may affect the properties tested in paste and concretes were carried out. Tests on cement paste combinations in order to investigate their developing properties and structure were also made. These included setting times; indicating the effects of the additional materials on the retardation acceleration of setting paste and also mercury intrusion porosimetry (MIP) in order to examine the effects of the materials on the porosity and critical pore diameter with the different materials. It is suggested that water will flow through the larger capillary pores more easily than the smaller gel pores (*Neville, 1995*) and the size of the pores can be affected by the w/c ratio (*Mehta & Monteiro, 2006*). Both concrete and paste samples were cured under the same conditions at 20^{o}C (± 1^{o}C) and removed after a specific number of days (3, 7, 28 days etc) to test strength, permeation and durability properties.

It was decided early on during the development of the experimental programme to test all combinations in concrete at 0.35, 0.5 and 0.65 w/c ratios, to cover those typical ranged in standards and the literature reviewed, with a fixed water content of 165 l/m^3, providing a range of strengths. For the cement paste phase 0.35 and 0.5w/c ratios were tested. The 0.65 w/c ratio was excluded from this due to likely problems with excessive bleeding of water from the samples and instability.

The range of tests carried out was based on a number of British Standards, American Society for Testing and Materials (ASTM) methods and tests that had been adopted in the literature reviewed. As these are well established, this enabled comparison with related studies, with information on their precision generally known. Fresh properties, plastic density

and slump, were tested as a matter of standard practice during casting of the concrete samples. For the paste samples standard consistency of the combinations was undertaken in order to determine their influence on water requirements and allow for calculation of packing density of each paste combination by using the De Larrad model.

Concretes were tested in order to examine the influence of the ternary materials on the strength, permeation and durability properties. Permeation tests carried out included initial surface absorption and sorptivity tests that required no pressure being applied to force the liquid into the concrete. Air pressure and water penetration under pressure tests were also carried out. Durability of the concretes was examined by accelerated carbonation and rapid chloride penetration tests.

It was also in the scope of this study to examine how the ternary concretes can influence environmental impact. This was carried out by making comparisons of calculated embodied CO_2 (ECO_2) for each of the concrete mixes, based per tonne of production, with the various properties of the concretes measured.

1.4 Outline of Thesis

Whilst this initial chapter has provided an introduction and a basic overview of the pressures facing the global industry to provide context to the research carried out, subsequent chapters will cover greater detail of specific elements of the research.

Chapter 2 will essentially consider previous studies of binary and ternary blended cements and illustrate the current understanding of the properties of the materials used within the cement combinations of interest. Whilst the benefits of using each material will be discussed it will be made evident from this chapter the limited number of studies carried out on ternary mixes combining GGBS with fly ash or limestone.

Chapter 3 provides a detailed account of the materials and sample preparation together with the test methodology used during the experimental phases for both paste and concrete, referring to relevant standards and sources where applicable. Subsequent chapters then review the results from these tests.

Chapter 4 examines the fresh properties of both the cement pastes and the concrete mixes, looking at the setting time, viscometery and the effects of the materials on superplasticiser dosage. This chapter also examines the early strength gain of the concrete mixes.

Chapter 5 examines strength development discussing the effects of each material, up to 180 days. Data obtained from the strength tests was used to consider binder cementing efficiency and the required w/c ratio for each combination to attain an equivalent strength of 40 N/mm^2 at 28 days is also determined and discussed. This chapter also examines the effects of void ratio of concrete on the resulting properties.

With the strength of the concretes discussed, ***Chapter 6*** moves on to investigate the permeation process, covering initial surface absorption and sorptivity. The effects of the various cement combination concretes on these properties are quantified. The influence of strength and critical pore size on these properties is also discussed. The air permeability and water penetration under pressure tests are discussed in ***Chapter 7***.

The results of the accelerated carbonation tests and rapid chloride tests on selected concrete mixes are discussed in ***Chapter 8***.

Chapter 9 discusses the impact of cement production at greater length whilst examining the embodied CO_2 (ECO_2) of all the concretes and their ability to reduce these levels and associated effects on strength and durability. The basic material costs of concrete production in an on-site context will also be discussed.

Chapter 10 presents the overall conclusions from this study and summarises the practical implications of using ternary cement combination concrete in a global construction industry. It will also make recommendations for future research in this area.

CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction

Despite a continuing growth in studies of blended cements, the focus of these is mainly dominated by binary cements, i.e. Portland cement with a single addition, either fly ash or ground granulated glass blast-furnace slag (GGBS). A comprehensive search of the literature found that there continues to be little coverage on the effects, and indeed the benefits, of ternary blended cements. Regardless, however, of this lack of evidence the use of blended cements is not a new chapter in the history of the cement due to increasing pressures to be sustainable. Bukki (*1986*) reports that blended cements were used in Italy as early as 1929.

Many authors have reported on the effects of binary cements and whilst these materials are becoming more wide and varied with the use of "by product" materials having increased *(Massazzi, 1987)* it are the effects of GGBS that are the focus of this study, more specifically its use within ternary blended cement with either fly ash or limestone. There have also been limited studies on ternary cements but there is little evidence of comprehensive studies combining fresh engineering and durability property tests. Given that all aspects of the service environment must be considered when designing a concrete *(Mehta, 1989),* this is needed if these materials are to be included in standards and find wider acceptance *(Hendricks, 2005)*.

This chapter will begin by briefly examining the hydration and reaction characteristics of the materials together with the influence of the materials used, on the properties of the concrete in this study, before reviewing their coverage within British and European standards. A summary of the effects of binary blended cements with Portland cement and GGBS as the main constituents are also included. Given that ternary cements incorporating fly ash and limestone as the third cementitious addition is the main focus of this study, these too will be covered where possible (with the limited studies available).

2.2 Influence of Different Additions of the Properties of Concrete

2.2.1 GGBS

The first commercial use of slag-lime cement was in Germany in 1865 following the discovery of its latent hydraulic properties in 1862 by Emil Lang (*Bijen 1996*). Its use has been on the rise for over 40 years (*Massazzi, 1987*) with slag cement being produced in many European countries (*Detweiler et al, 1996*). The production and utilisation of GGBS for a number of countries is reported by Mehta in Detweiler et al (*1996)* and is summarised in Table 2.1.

Table 2.1: The production and utilisation of GGBS globally [Source: Mehta, 1989 in Detweiler et al (1996)]

Country	Production (million tonnes)	Utilisation (million tonnes)
UK	4.0	4.0
USA	13.0	1.0
Canada	2.9	2.0
China	22.0	16.0
France	10.4	1.9
Germany	15.0	2.8
South Africa	1.5	0.6
India	7.8	2.8
Japan	24.0	8.2

Chemically GGBS is a mixture of lime, silica and alumina and is of similar oxide composition as Portland cement (PC) but in different proportions (*Civil & Marine, 1993*). These differences in proportions are shown in Table 2.2 where the figures were adapted from ACI 226 (*1987)* and include the typical oxide composition for GGBS from Civil & Marine (*1993*). As with many materials the oxide composition of GGBS can vary. Table 2.3 summarises the composition of GGBS found within the literature (these provide an overview from 1992 to 2008 and are indicative of changes that have occurred).

Table 2.2: Typical oxide composition of GGBS [Source: ACI 226 (1987), Civil & Marine, (1993)]

	Composition (%by Mass)	
Oxide	ACI, 1987	Civil & Marine, 1993
SiO_2	32-40	35
Al_2O_3	7-17	11
FeO_3	0.1-1.5	1
CaO	29-42	41
MgO	8-19	–
SO_3	0.7-2.2	–

Table 2.3: Oxide composition of GGBS found within literature

Chemical composition, (%)	Sivasundaram & Malhotra (1992)	Lane & Ozyildirim (1999)	Bleszynski et al (2002)	Khatib & Hibbert (2005)	Sharfuddin et al (2008)
SiO_2	38	37.6	35.28	36	34.1
$Al2O_3$	6.63	3.3	9.71	9	13.2
Fe_2O_3	0.4	0.4	0.56	1	0.7
CaO	35.7	17.6	40.47	43	41.8
MgO	13.6	11.2	8.76	7	6.3
SO_3	–	1.94	3.79	-	2.4

Influences of Fresh Properties

The presence of GGBS in a concrete mix improves workability making the mix cohesive yet mobile (*Day 1999*). This is aided by the GGBS, whilst its fineness can be similar to that of PC it is less dense, which can allow more coarse aggregate to be used reducing the cohesiveness of the mix thus improving the workability. The cohesiveness is reduced due to the lower water demand caused by better dispersion of the cement by the smoother GGBS; with Day (*1999*) referring to GGBS as having a glassy surface that reduces water demands. Tattersall (*1991*) found that the surface texture affects water demand. A higher GGBS content gives further improvements (*Meusel & Rose, 1983*) and allows reduced water contents (*Stutterheim 1968,* in *Detweiler et al, 1996*). Roy et al (*1982*) reported that these effects were less than those found in fly ash blended cements. The previously discussed slower reactivity is also indicated by an increase in setting time which is extended with greater GGBS content (*Sivasundaran &*

Malhotra 1992). It is suggested that this increase is in the region of 10 to 20 minutes for each 10% addition of GGBS (*Hogan & Meusel, 1991*).

Previous research has indicated that the early stages of development of compressive strength of concrete containing a mix of PC and GGBS can be lower than a PC concrete control depending on how they are proportioned (*Wimpenny et al 1989*). Mehta (*1986*) implied that this is generic of pozzolanic cements as they are slower to develop strength than Portland cements, more noticeably so in colder climates (*Nepper-Christensen, 1979*). Chern and Chan (*1989*) believe that this can be overcome by varying the proportion of PC and GGBS and whilst the rate of strength development is lower with higher GGBS levels strength is gained at later stages and can exceed that of the control PC concrete beyond 28 days (*Hogan & Meusel 1981*). Increasing the GGBS level of cement by 30-50% by mass can increase the strength of the concrete from 7 days (*Meusel & Rose, 1983*). Elahi et al's (*2010*) more recent study found that a 50% GGBS binary mix was comparative to the CEM I control mix at 28 days, at the early age strengths it was 74% of the CEM I strength at 3 days, increasing to 95% at 7 days. By increasing the GGBS level to 70% the strength decreases considerably to 74% of the CEM I mix at 28 days. Elahi et al also test fly ash mixes at 20 and 40% levels. The 20% level gave better strength results than the 50% GGBS level only at 3 and 7 day testing, at 28 days the strength of the 20% fly ash mix is considerably less than the 50% GGBS.

2.2.3 Fly Ash

As with GGBS the use of fly ash to form blended cements has been carried out for many years and brings several benefits to concrete such as workability enhancement, durability and strength (*Detweiler et al, 1996*). Fly ash is an industrial by-product derived from the exhaust gases of coal-fired power stations. Given the global extent of such power stations the availability of fly ash is extensive and whilst many countries are realising the potential of fly ash in concrete others are still sending most of it to landfill. Alonso & Wesche (*1992*) reported on the global production and utilisation of fly ash in 1992 and this has been summarised in Table 2.4. Since then production in the UK reduced to approximately 6.2 million tonnes (*UKQAA, 2002*) in 1997 and currently stands at 4.59 million tonnes for 2010 (*Sear, 2011*). Figure 2.1

indicates the percentage of use within the construction industry across Europe based on the most recently available production figures from ECOBA for Europe.

Table 2.4: The global production and utilisation of fly ash [Source: Alonso & Wesche, 1992]

	1992	
Country	**Production (million tonnes)**	**Utilisation (million tonnes)**
UK	10.4	5.9
USA	38.3	8.0
Canada	3.2	1.1
China	41.0	9.5
France	2.2	1.3
Germany	2.9	2.2
South Africa	10.4	0.6
India	39.0	1.2
Japan	3.3	0.9

Detweiler et al (*1996*) report that between 1977 and 1996 the use of fly ash in concrete tripled but significant quantities are still disposed of. This low use of fly ash is mainly due to its low quality and composition which can make it unsuitable to be blended with cements. Ashes from some plants in India have high carbon content; ASTM C 618 states that fly ash for concrete should not exceed 5.0% of carbon. Given that loss of ignition (LOI) tests are stated to indicate carbon content (*Neville, 1995*) BS EN 450-1 (*2005*) is the current standard and specifies this upper limit in the UK to be 7.0%. These standards, however, include different categories of fly ash. Category A has an LOI of less than 5% whilst Category B has a range of 2-7% which is permitted for use within the UK as it lies within the upper limit specified in BS EN 450-1 of 7%. Category C therefore is not permitted for use in concrete as it has an LOI range of 4-9%. The chemical composition of fly ash is different to that of both GGBS and Portland cement. Table 2.5 shows a summary of the oxide composition of fly ash found within the literature. For low lime fly ashes there is a requirement for the combined SiO_2, Al_2O_3 and Fe_2O_3 to be greater than 70%.

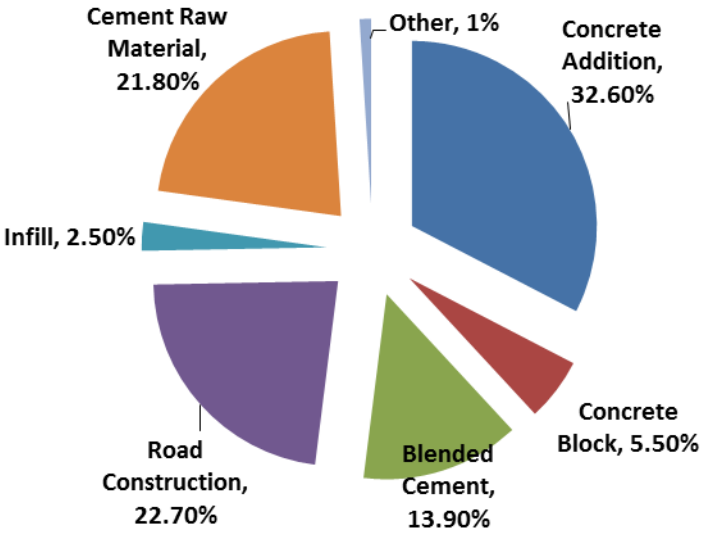


Fig 2.1: Utilisation in the construction industry and mining in Europe in 2008 – 17.6 million tonne used. (ECOBA, 2011)

Table 2.5: Oxide composition of fly ash found within literature

Chemical composition, (%)	Shehata et al (1999)	Hasssan et al (2000)	McCarthy et al (2001)	Long et al (2005)	Eliha et al (2010)
SiO2	41.96	49.9	41.3	57.6	50.7
Al2O3	19.64	26.5	40.7	30.8	28.8
Fe2O3	20.07	8.1	5	5.8	8.8
CaO	5.57	1.7	2.5	3	2.38
MgO	1.19	1.3	0.5	1.5	1.39
SO3	0.95	0.9	0.2	1.3	2.4

The spherical particles of fly ash can assist in reducing the water requirement resulting in a more cohesive mix this is further supported by the work of Long et al, (*2005*). Long et al (*2005*) also report on the influence of fly ash on the workability as well as the strength and durability of the concrete. Hassan et al (*2000*) studied the strength of a variety of mixes with fly ash and found that until 28 days the strength of a 30% fly ash blended cements were lower than the Portland cement control mix, but matched at 28 days before exceeding the strength of

ordinary Portland cement. This depends on how mixes are proportioned and the water cement ratio required to achieve certain strengths. Elahi et al (*2010*) however, found that fly ash binary mixes were markedly lower in compressive strength than the Portland cement mixes at 28 days. A 20% fly ash binary concrete was 74% of the CEM I control mix while a 40% fly ash binary concrete had only 58% of the strength of the Portland cement control. There is limited information on the use of fly ash, combined with GGBS, in ternary cement combination concretes.

2.2.4 Limestone

It was assumed until the 1980's that limestone was an inert filler within concrete (*Ramezanianpour et al, 2009*). Studies subsequently found that limestone has several effects. Ramachandran & Zhang (*1986*) observed that the addition of $CaCO_3$ from limestone accelerates hydration of Portland cement by providing nucleation sites and this effect on the structure of the hydrated cement paste can be beneficial. It was also found that limestone becomes incorporated into the C-S-H phase, affecting the structure of the hydrated cement paste (*Ramachandran, 1984*). Within the Portland cement composition 5% limestone is permitted by European standards (*BS EN 197-1, 2000*) as a minor addition constituent (MAC) as well as American publications (*ASTM C 150-04*) quantities above this level gives Portland limestone cements containing 6-35% limestone.

Following a study in 1996, Nehdi et al found that the benefits of using fillers such as limestone is mainly to improve the cost effectiveness of cement (*Nehdi et al 1996*) yet in a later study it was shown that the workability and stability of fresh concrete were also improved (*Nehdi et al 1998*) with these fitting between the cement grains, reducing the space for water and thus decreasing water demand and increasing plasticiser efficiency (*Gallias, 2000*). A study into the effects of limestone additions by Brookbanks (*1989*) considered introducing limestone in the range of 5-28% to a cement blend. It was concluded that the water demand was only marginally reduced with increasing filler content, with no difference in water demand at the 5% filler level.

A greater increase in the limestone content was found to reduce the water demand, CEM I gave a water demand of 26%, by replacing 35% with limestone the water demand was reduced to 22.8% (*Tsivilis et al, 2002*) confirming Vuk et al's (*2001*) study that found a 5% increases in limestone decreased water demand for a standard consistency by 0.5. Both authors discuss the fineness of limestone as an important factor affecting water demand stating that higher fineness reduces water demand. The addition of limestone to the cement mix does not replicate the improvements to compressive strength found with both GGBS and fly ash. A 10% addition does not show noticeable reductions (*Tsivilis et al, 2002* and *Ramezanianpour et al, 2009*) when compared to the CEM I mix. However as greater volumes of limestone are added more significant decreases in strength are seen, as much as 23 N/mm^3 at 28 days for 35% limestone level. Again the effects of fineness were seen; finer limestone increased the strength for each of the test ages. Tsivilis et al, (*2002*) compare makes of CEM I to limestone binary mixes with additions of 10, 20 and 35% all material was ground for 38, 42, 52 and 60 minutes thus increasing the fineness of each material.

A number of studies have been carried out on the permeability of limestone cements. Tsivilis et al (*1999*) concluded that limestone additions can improve the permeation properties of concrete with the mean pore size of concrete specifically affecting sorptivity and gas permeability (*Tsivilis et al, 1999*). A subsequent study confirmed this and found that water permeability also improved with limestone content and it was also concluded that a limestone content of 15% did not affect porosity (*Tsivilis et al, 2003*). Pipilikaki & Beazi-Katsioti (*2009*) studied the porosity and particle size distribution of limestone Portland cements using mercury intrusion porosity (MIP) and concluded that limestone changes the pore structure, increasing the capillary pore size from 20nm to 40nm when a 30% limestone level was used, this being the maximum permitted by BS EN 197-1.

2.3 Hydration & Reaction Characteristics of Cement & Cement Additions

2.3.1 Portland Cement

Due to the importance, and indeed the complexity of hydration of cement and the reaction of additions, it would be prudent to examine this process separately so as to understand the basic principles involved.

Hydration occurs when water is added to cementitious materials and involves a series of irreversible chemical reactions, during which cement paste sets and hardens (Taylor et al, 2006). It is the mineral compounds, specifically the silicates and aluminates, that react with the water to form hydrates (Neville & Brooks, 2007). Mehta & Montiero proposed two mechanisms of hydration. During the early stages through solution hydration occurs involving the dissolution of anhydrous compounds into their ionic constituents. Hydrates are said to form in the solution and the reorganisation of these constituents also occurs. When this ionic mobility becomes restricted topochemical, or solid state, hydration takes place at the surface of the anhydrous cement, aiding in the hydration of the residual cement particles.

For hydration to occur, however, it is the compounds of the materials that are key. Tricalcium silicate (C_3S) is the most prevalent mineral in Portland cement and contributes to most of the early strength development with the formation of portlandite and C-S-H gel.

$$C_3S + 6H \rightarrow C_3S_2H_3 + 3Ca(OH)_2$$

[Eq 2.1]

Dicalcium silicate (C_2S) is also present in the cement and its hydration results in the same products but with the relative amount of $Ca(OH)_2$ being less. Its rate of hydration is slower than C_3S as it is less soluble and whilst its contribution to early strength is minimal, it does contribute significantly to later strength.

$$2C_2S + 4H \rightarrow C_3S_2H_3 + Ca(OH)_2$$

[Eq 2.2]

The aluminates are faster to react than the silicates, despite being lower in content in Portland cement. C_3A is more soluble than C_3S, and reacts almost immediately despite being more complex and involving a number of reactions that need to take place (Taylor et al, 2006).Calcium aluminate hydrates form with an initial, rapid reaction that can release large

amounts of heat and result in the setting of the cement paste within minutes, referred to as a flash set (Neville & Brooks, 2007), reducing the workability of the concrete drastically.

$$2C_3A + 21H \rightarrow C_3AH_{19} + C_2AH_8 \rightarrow 2C_3AH + 9H$$

[Eq 2.3]

In order to prevent flash setting, however, gypsum (CSH_2) is added during the production of cement. It is also highly soluble and releases calcium and sulfate into the pore solution, a different reaction occurs when combined with the C_3A with the hydration product ettringite being formed.

$$2C_3A + 3CSH_2 + 26H \rightarrow C_6AS_3H_{32}$$

[Eq 2.4]

As there is insufficient gypsum to react with all of the C_3A, the resulting ettringite reacts with the remaining C_3A to form monosulfoaluminates, particularly if more than 5% C_3A is present in the Portland cement.

$$2C_3A + C_6AS_3H_{32} + 4H \rightarrow 3C_4ASH_{12}$$

[Eq 2.5]

Neville & Brooks (2007) use a simple schematic representation of the hydration process (Figure 2.2), whilst Taylor et al (2006) break the process down into five stages related to the heat development during hydration. As stated by Way & Lee (2010), hydration is an exothermic process that is indicative of many chemical reactions. Given that cement is a heterogeneous mix of compounds, the hydration process itself consists of a number of reactions occurring simultaneously, albeit at different rates that are made even more complex with the inclusion of additional materials.

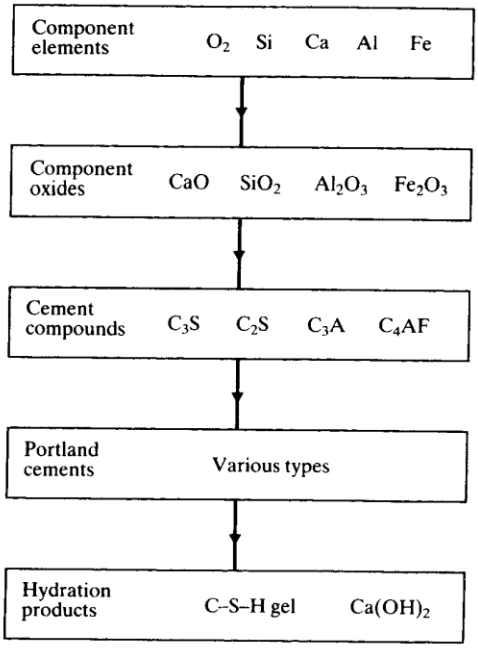


Fig 2.2: Schematic representation of cement hydration (Neville & Brooks, 2007 p14)

2.3.2 GGBS

In respect of GGBS the reaction or hydration occurs initially due to the presence of lime [$Ca(OH)_2$] that has been freed by the hydration of Portland cement:

$$Ca(OH)_2 + SiO_2 + H_2O \rightarrow CSH\ gel$$

[Eq 2.6]

Gao et al (2005) state that the reaction of GGBS starts at an early age and involves the consumption of $Ca(OH)_2$. The fineness of GGBS tends to be slightly higher than that of PC and whilst its performance in concrete as a blend is similar to that of a PC-fly ash cement, the reaction process differs in that initially these are slow due to the dependency of the breakdown of glass by hydroxyl ions released during the hydration of PC. Hydration of C_3S in PC is delayed in the first instance, but accelerated during the later ages (Ogawa et al, 1980). Miura & Iwaki (2000) and Aldea et al (2000) suggest that the reaction of GGBS with Portland cement involves a two-stage reaction. The first and predominant reaction is with alkali hydroxide, and those that follow allow for a long-term gain in strength (Hogan & Meusel, 1991). The rate of

hydration is therefore dependent on its glass content (Tanaka et al 1983) and chemical and physical properties (Roy & Idorn, 1982).

Li et al (2003) state that the hydration rate of GGBS and fly ash combined is greater than fly ash alone, indicated by a lack of hydrated fly ash particles at seven days by SEM. Whilst Swamy & Boukni indicated that GGBS was slower to react, Li et al showed that when incorporated with fly ash, the rate of hydration increased at an early age (Swamy & Boukni, 2000; Li et al, 2003). A secondary calcium silicates compound is produced when the GGBS reacts with the $Ca(OH)_2$, this together with the ettringite and remaining $Ca(OH)_2$ act as nucleation sites, leading to an increase in the hydration rate of fly ash. The GGBS also releases OH- ions and alkalis into the pore solution, aiding in the break-down of the glass phase of fly ash, by reacting with the SiO_2. The pozzolanic reaction of the fly ash, as with the reaction of GGBS, reduces the content of $Ca(OH)_2$ but according to Voglis et al (2005), the fly ash may contribute to the formation of C_2AH_8 due to the release of Al_2O_3.

A more recent study by Narmluk & Nawa (2011), states that the inclusion of fly ash has a diluting effect on the hydration of cement. This is in addition to a physical effect at an early age and a chemical effect. Hydration only take places in water filled capillaries and a loss through evaporation can occur if not prevented (Neville & Brooks, 2007). The dilution effect suggests that the fly ash increases the effective w/c ratio, resulting in enhanced long-term hydration due to increased water availability within these capillaries. The physical effect of fly ash discussed by Narmluk & Nawa refers to the retardation related to the condition of the surface of the fly ash which is referred to in a number of other studies (Ogawa et al, 1980; Rahhal & Talero, 2004). Interestingly Narmluk & Nawa contradict this and state that there is also a physical acceleration effect, as its surface provides additional nucleation sites. The chemical effect of fly ash has already been indicated by the consumption of $Ca(OH)_2$ by this and GGBS, resulting in a lower concentration, which would aid in the acceleration of the dissolution of Ca^{2+}.

2.4 Coverage of Cement Additions in BS EN 197-1 and BS EN 206/ BS 8500

In the mid 1970's up to 20 different cements were being utilised across the EEC and by the 1990's this number had increased to over 50, following an enquiry by the CEN/TC51(the technical committee responsible for preparing cement standards). The cements being used were dependent on the source of raw materials, different climate and building techniques being used across Europe and due to its flexibility similar cements could be applied to different structures that create differing requirements placed on its performance in specific environments, for example coastal locations.

Due to the vast number of cements being used it became necessary to 'separate the common cements' from 'special cements' that were to be evaluated in accordance with further British Standards such as the BS EN 196 series. The Committee's work in evaluating these cements led to the BS EN 197 series of standards *"Cement – Composition, specification and conformity criteria"* that include common cements (Part 1), conformity evaluation (Part 2), low heat common cements (Part 3) and sulphate-resisting cements (Part 4). This review focuses on BS EN 197-1.

BS EN 197-1 defines "27 common cements and their constituents" specifying the composition, requirements and conformity criteria for common cements which also includes cements with low heat of hydration following an amendment in 2004. The "constituents" outlined in this standards may fall into two categories; main constituents that will exceed 5% by mass and minor additional constituents that will not exceed 5% by mass. To clarify, the materials defined as constituents in BS EN 197-1 are referred to as "additions" by BS EN 206-1. The former standard defines the proportion of each constituent over a range of six strength classes, stating that each must meet a number of requirements (in accordance with the BS EN 196 series) including mechanical, physical and chemical, and covers five main cement types from CEM I (Portland cement) to CEM V (composite cement). Each cement type is notated to indicate, in addition to cement type, the proportion of cement clinker, a second main constituent, standard strength class and the rate of early strength gain.

Table 2.6: The 27 products in the family of common cements from BS EN 197-1

Main types	Notation of the 27 products (types of common cement)		Composition [percentage by mass [a)]]										
			Main constituents										Minor additional constituents
			Clinker	Blast-furnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone		
						natural	natural calcined	siliceous	calca-reous				
			K	S	D [b)]	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM I	95-100	–	–	–	–	–	–	–	–	–	0 to 5
CEM II	Portland-slag cement	CEM II/A-S	80 to 94	6 to 20	–	–	–	–	–	–	–	–	0 to 5
		CEM II/B-S	65 to 79	21 to 35	–	–	–	–	–	–	–	–	0 to 5
	Portland-silica fume cement	CEM II/A-D	90 to 94	–	6 to 10	–	–	–	–	–	–	–	0 to 5
	Portland-pozzolana cement	CEM II/A-P	80 to 94	–	–	6 to 20	–	–	–	–	–	–	0 to 5
		CEM II/B-P	65 to 79	–	–	21 to 35	–	–	–	–	–	–	0 to 5
		CEM II/A-Q	80 to 94	–	–	–	6 to 20	–	–	–	–	–	0 to 5
		CEM II/B-Q	65 to 79	–	–	–	21 to 35	–	–	–	–	–	0 to 5
	Portland-fly ash cement	CEM II/A-V	80 to 94	–	–	–	–	6 to 20	–	–	–	–	0 to 5
		CEM II/B-V	65 to 79	–	–	–	–	21 to 35	–	–	–	–	0 to 5
		CEM II/A-W	80 to 94	–	–	–	–	–	6 to 20	–	–	–	0 to 5
		CEM II/B-W	65 to 79	–	–	–	–	–	21 to 35	–	–	–	0 to 5
	Portland-burnt shale cement	CEM II/A-T	80 to 94	–	–	–	–	–	–	6 to 20	–	–	0 to 5
		CEM II/B-T	65 to 79	–	–	–	–	–	–	21 to 35	–	–	0 to 5
	Portland-limestone cement	CEM II/A-L	80 to 94	–	–	–	–	–	–	–	6 to 20	–	0 to 5
		CEM II/B-L	65 to 79	–	–	–	–	–	–	–	21 to 35	–	0 to 5
		CEM II/A-LL	80 to 94	–	–	–	–	–	–	–	–	6 to 20	0 to 5
		CEM II/B-LL	65 to 79	–	–	–	–	–	–	–	–	21 to 35	0 to 5
	Portland-composite cement [c)]	CEM II/A-M	80 to 94	<---------- 6 to 20 ---------->									0 to 5
		CEM II/B-M	65 to 79	<---------- 21 to 35 ---------->									0 to 5
CEM III	Blastfurnace cement	CEM III/A	35 to 64	36 to 65	–	–	–	–	–	–	–	–	0 to 5
		CEM III/B	20 to 34	66 to 80	–	–	–	–	–	–	–	–	0 to 5
		CEM III/C	5 to 19	81 to 95	–	–	–	–	–	–	–	–	0 to 5
CEM IV	Pozzolanic cement [c)]	CEM IV/A	65 to 89	–	<---------- 11 to 35 ---------->					–	–	–	0 to 5
		CEM IV/B	45 to 64	–	<---------- 36 to 55 ---------->					–	–	–	0 to 5
CEM V	Composite cement [c)]	CEM V/A	40 to 64	18 to 30	–	<-------- 18 to 30 ------>			–	–	–	–	0 to 5
		CEM V/B	20 to 38	31 to 50	–	<-------- 31 to 50 ------>			–	–	–	–	0 to 5

[a)] The values in the table refer to the sum of the main and minor additional constituents.
[b)] The proportion of silica fume is limited to 10 %.
[c)] In Portland-composite cements CEM II/A-M and CEM II/B-M, in Pozzolanic cements CEM IV/A and CEM IV/B and in composite cements CEM V/A and CEM V/B the main constituents other than clinker shall be declared by designation of the cement (for example see clause 8).

The five types of cement are summarised in Table 2.6, extracted from BS EN 197-1. In addition to Portland cement clinker (K) the other main constituents covered by the standard include GGBS (S), natural and natural calcined pozzolana (P/Q) covering metakaolin, siliceous and calcareous fly ash (V/W), limestone (L/LL) and silica fume (D). The standard also includes burnt shale (T). The same materials may also be regarded as "minor additional constituents" if their mass in cement does not exceed 5%.

As previously stated BS EN 206-1 specifically defines additions in Section 3.1.23 as *"finely divided inorganic material used in concrete in order to improve certain properties or to achieve special properties"* and further refers to two types of addition; Type 1, nearly inert and Type II, pozzolanic or latent hydraulic. BS EN 206-1 states that both Type I and II additions may be used in concrete in quantities, as per the initial tests outlined in Annex A of the standard.

The standards are also referred to for calculating water/cement ratio. BS EN 206-1 contains specific references to fly ash and silica fume and permits other procedures if their suitability can be established. This standard also refers to combinations and defines a combination as follows:

> *"Restricted range of Portland cements and additions which, having been combined in the concrete mixer, count fully towards the cement content and water/cement ratio in concrete."* (BS 8500 Section 3.1.2)

The restricted range of combinations included in BS EN 197-1, it incorporates CEM I cements of standard strength class 42.5 or more with fly ash (to BS EN 450-1), GGBS (to BS 6699), limestone (to BS 7979) and fly ash (to BS 3892-1). BS 8200-2 Annex A defines the early stage and 28 day strength that these combinations must fulfil, as well as outlining the range of combination proportions that can count towards the cement and water/cement ratio. BS 8500 covers restrictions on the type and proportion of additions for use in designed, designated and standardised prescribed concretes.

2.5 Particle Packing

It is considered that particle packing is fundamental for strong durable concrete. The fineness of additions, GGBS, fly ash etc., are not too dissimilar to PC but appear to allow for better packing and, when these mixes are properly cured, the result is not only improved strength but also durability (*Nehdi & Rahman, 2004*). The cement particles are deflocculated, dispersed by the smaller particles that then fill the voids creating a denser, and therefore stronger, material. The packing of the concrete particles, or fines, can be equally important as the aggregate within the concrete structure (*Wong & Kwan, 2008*). Studies on the particle packing of concrete systems date back as far as Feret in 1892 (*Dhir et al, 2002*). Feret studied the influence of particle size distribution on the properties of concrete from particle packing and determined that to obtain high quality concrete there should be suitable distribution of different size particles to achieve maximum packing (*Aiquin et al, 1999*). This principle was more recently studied by Nui et al (*2002*) who concluded that in order to provide high performance concrete well packed particles are important in order to produce "a mixture that has a wide size distribution and low void space between their particles…" that will enhance the microstructure (*Nui et al, 2002*).

Studies over the years have resulted in a number of models for calculating voids ratio or particle packing density. Furnas developed a model in 1929 which progressed over time by Aim & Goff in 1967, Toufar in 1976 and Dewar in 1992. Dhir et al discuss these models in detail together with the Stoval & de Larrad model who contributed the linear packing (LPM) and compressible packing models (CPM). The latter was developed in 1999 by De Larrad and is a refined version of the previous LPM (*Jones et al, 2002*).

The use of finer materials within the mix design increases the variety of particle sizes. Silica fume and metakaolin for example, are able to fill spaces between cement particles creating a denser packing material as illustrated in Figure 2.4 from Taylor (*1990*). The best packing occurs with these finer particles filling exactly the void spaces between larger particles.

The fineness of materials and their effects on packing density have led to a number of studies into the effects on water demand. Wong & Kwan (*2008*) concluded that the smaller

finer particles took the place of water in the pore spaces thus reducing the water demand. This contradicted Stutzman & Centeno's earlier study in 1995 who found that the higher surface areas of the finer particles resulted in greater water demand and ultimately lowered the strength of the concrete. Such contradictions may be the result of different mixing techniques and the inclusion of superplasticisers as well as the diversity of particle sizes and shapes within the cement system. Jones et al (*2003*) reported that finer fillers significantly affect the packing in mixes using plasticizers and angular fillers can increase the voids ratio in non-plasticized mixes.

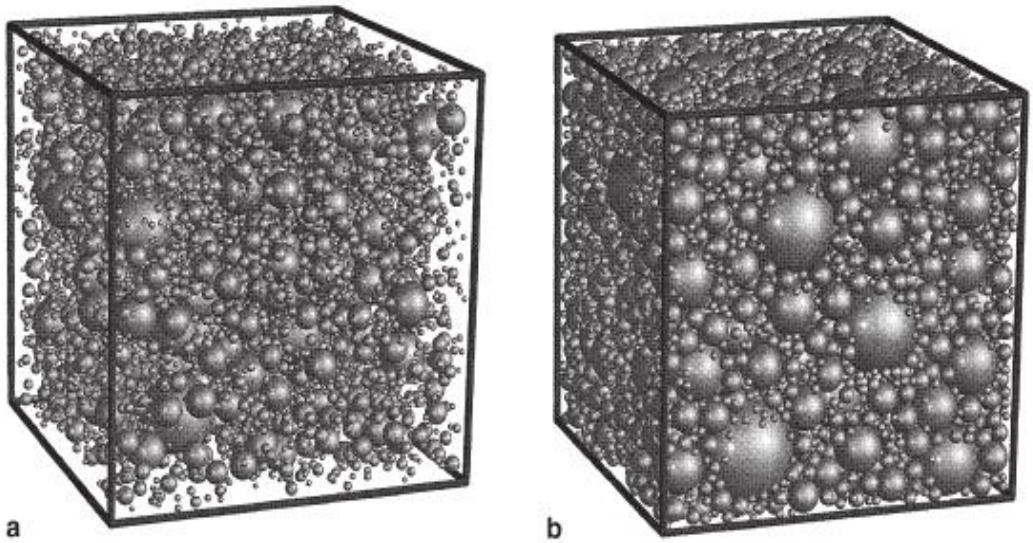


Fig 2.4: a) loosely packed particles; b) denser material

(Source: Taylor, 1990)

2.6 Binary Blended Concretes and Their Properties

2.6.1 Fresh Properties

Taylor & Smith (*1988*) refer to workability as the most important term relating to fresh (plastic) concrete. Workability is defined as the property of concrete that determines its ability to be placed, compacted and finished. Compaction is important since the consequences of inadequate compaction can be serious (*Taylor & Smith, 1988*). The addition of slag within a

concrete blend will produce a higher workability concrete due to its smoother surface texture (*Tattersall, 1991*). On a weight-for-weight basis for a given replacement of GGBS, there is an increase in powder volume because its specific gravity is lower than that of Portland cement.

A GGBS concrete will demand less water for cohesiveness, flow and compaction characteristics, to that of a CEM I concrete. This reduction in water content for a constant workability is influenced by the percentage of GGBS and the total cementitious material content (*Sivasundran & Malhotra, 1992*) and reduction of the order of 5% can be expected according to Tattersall (*1991*). Whilst Day (*1999*) confirms Tattersall's findings that it is the surface texture of the GGBS that affects the water demand, referring specifically to its glassy surface Day suggests that the water requirement is only slightly changed. Bijen (*1996*) stated that there was no significant difference from CEM I concrete in the workability, pumpability and compactability of the GGBS concrete.

It was previously shown by Sivasundran & Malhotra (*1992*) that the setting time increases with GGBS content, indicative of a slower reactivity, confirming the findings of Fulton (*1974*). Brooks et al (*2000*) stress that the setting characteristics of cement mix is important in the field of construction in order to schedule the stages of construction on site from the transportation of concrete to the finishing. These characteristics can aid in the decision of whether or not to use a retarding admixture or accelerator. The setting time of concrete is affected by a number of factors including water/binder ratio, initial and curing temperatures and type of admixtures (*Ramachandran et al, 1995*).

Whilst there is a general consensus that GGBS retards the setting time there have been contrasting opinions with regard to the effect of silica fume in binary mixes. Khedr & Abou-Zeid (*1994*) and Alshamsi et al (*1997*) both agree that silica fume does effect the setting time, with retardation increasing with replacement level. These findings dispute an earlier study by Pistelli et al in 1984 that indicate that there were negligible effects. The influences of metakaolin were studied in addition to those of silica fume by Brooks et al (*2000*) and they concluded that both retarded setting time. Figure 2.5 shows the settings times recorded for three silica fume concrete mixes, with increasing silica fume volumes, when compared to Portland cement

(OPC). There was clear indication that both initial and final setting times were extended as the level of metakaolin, specifically increased.

2.6.2 Strength Development

Wimpenny et al (*1989*) recorded that the rate of compressive strength development during the early stages of a concrete mix incorporating GGBS and cement was lower than that of the control PC samples. Swamy & Boukini however, suggest that proper mix design of GGBS concretes can produce comparable results by the third day (*Swamy & Boukini, 1990*). Whilst again it is the fineness of the material and the mix proportions used in the mix design that affect the development of strength of concrete (*Kokubu et al, 1989* and *Sivasundran & Malhotra, 1992*) other factors are also influential, such as the exposure temperature (*Chern & Chan, 1989*), water/binder ratio (*Swamy & Boukini, 1990*) and curing conditions (*Austin et al, 1992*).

Chern & Chan (*1989*) indicate that whilst fineness and exposure temperature are influential, varying the GGBS level can also affect the rate of strength development. Indeed at higher GGBS levels, the rate of strength development is lower, agreeing with the findings of Hogan et al (1981). Hogan et al also noted that the gain in strength at later ages exceeded that of PC alone, when compared beyond 28 days. Babu & Kumar (*2000*) studied the efficiency of GGBS in binary concretes (using similar evaluation methods to that of fly ash and silica fume) with levels of 10-80%. Data from earlier studies focusing on fly ash and silica fume binaries, as well as GGBS was collated and compared to give a representation of the cements manufactured at that time (2000). The study confirmed the strength development of previous research and indicated that an increase of water/cement ratio decreased strength as shown in Figure 2.6 (*Babu & Kumar, 2000*).

Muira & Iwaki's (*2000*) study reviewed the effects of curing method on the strength development of GGBS concrete at levels of 50-80% and three different fineness grades. The overall strength development followed similar trends to previous studies, but it was found that heat curing of GGBS improved early age strength without compromising that at later ages. This was not found in GGBS with a greater specific surface area (*Muira & Iwaki, 2000*). Rapid hydration at an early stage caused by heat curing, resulting in a poor microstructure of

hydrated cement paste in the finer GGBS, limiting reactions at later ages. A similar study tested BRECEM concretes using both water and air curing techniques for GGBS levels of 40, 50 and 60% (*Quillin et al, 2001*). A later study in 2006 by Barnett et al concluded that it is the reaction of GGBS that aids strength development and this is more sensitive to temperature than cement type (*Barnett et al, 2006*). The results of Barnett et al's tests on the effects of curing temperatures are shown in Figure 2.7. Their findings that higher early age temperatures enhance the strength development of GGBS concrete confirms those of Roy and Idorn (*1982*).

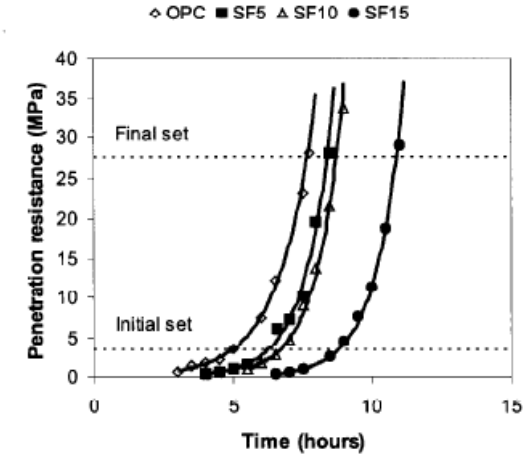


Fig 2.5: Influence of silica fume on the penetration resistance of concrete (Source: Brooks et al, 2000)

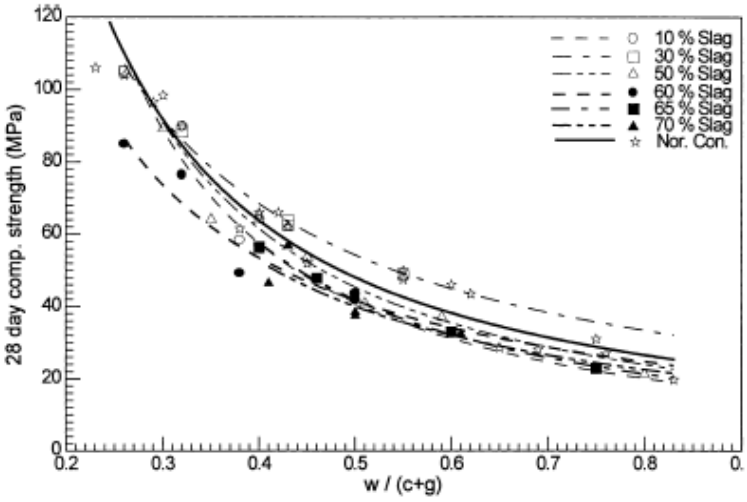


Fig 2.6: 28 day strength variation with w/CEM I+GGBS ratio (Source: Babu & Kumar, 2003)

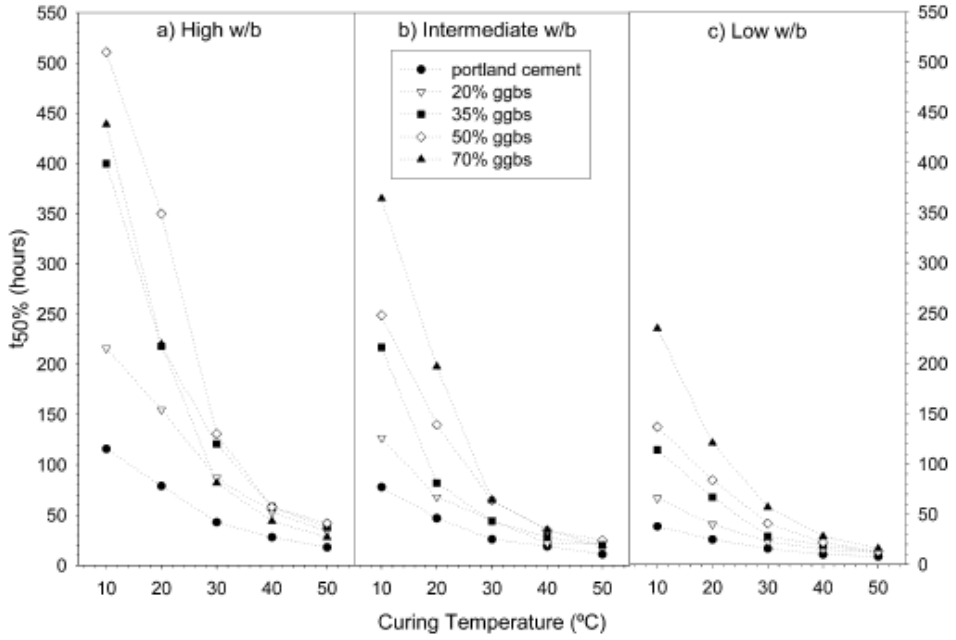


Fig 2.7: Effects of curing temperature on the time to reach 50% of ultimate strength (Source: Barnett et al, 2006)

2.6.3 Durability

It is important that concretes perform their intended function with regard to strength and serviceability (*Neville, 1995*)Given the diverse use of concrete it is fundamental that it must be able to withstand any number of factors that can affect its rate of deterioration. Not only does this include the permeation of fluids, but its rate of carbonation and resistance to chloride which represents the greatest threat to concrete.

Permeation Properties

In order to understand the behaviour of concrete with regards to deterioration that may occur it is appropriate to consider the transport processes that may be involved in these processes. Essentially there are four main transport processes: pressure driven flow; diffusion; electro-migration; thermal migration.

Pressure Driven Flow: Pressure driven flow, or permeability, as previously discussed, refers to the rate at which a liquid flows when pressure is applied. In some circumstances this pressure may be external, whilst in others it may depend on the absorption process itself that can create pressure differentials. It is likely that water itself and its ability to permeate concrete cause less significant damage than when chlorides and sulfates are present.

Diffusion: Diffusion refers to the process in which ions pass through saturated concrete without the flow of water and are driven by a concentration gradient. When a strong solution is in contact with a weaker one, they will both tend towards an equal concentration. For example salt will dissolve and create a uniform concentration throughout the water. This same mechanism will cause any ions present within the pore water of concrete to diffuse out.

Electro-migration: For electro-migration to take place a voltage difference, or electric field, needs to be present. This can be caused by the electrical potential of pitting corrosion on reinforcing steel and not necessarily from leakage from an external direct current power supply. When applied across concrete negative ions will move towards positive electrodes, e.g. chloride ions will be carried into the concrete or hydroxyl ions out of it.

Thermal Migration: Within concrete, water or ions will move from hot to cold regions at a rate dependent on the permeability of the material. This is not evaporation which occurs on the exposed surface of the concrete. If concrete has been contaminated by de-icing salts the salt saturated water in these surface pores will migrate rapidly into concrete, when it is heated by sunlight. Once it has entered concrete and begins to cool it is possible that diffusion will occur.

Capillary suction and osmosis: Though essentially transport processes themselves, these can reduce or increase the rate of the transport process. The former occurs in the fine capillary pores with wetting surfaces and is caused by surface tension. Concretes with a finer pore structure can experience greater capillary suction pressures thus increasing absorption. Capillary suction can be affected by the density, viscosity and surface tension of the liquid together with the angle of contact and the size of the capillary pores. The roughness of the concrete surface can influence the angle of contact so a regular test surface is beneficial. The

capillary pores may also be lined with absorbed water. Oven drying to a constant weight removes the internal moisture content but too severe drying can also cause micro-cracking. Ambient conditions may also influence the rate of absorption so it is important to standardise the conditioning, temperature of water and test conditions as a whole. Dias (*2004*) studied the effects of drying on concrete sorptivity and advised that 3 days at 50^{o}C oven drying would increase the sensitivity of the sorptivity without reducing its "discriminatory power" significantly.

Osmosis relies on a semi-permeable membrane through which water can pass but liquids or gases; etc., dissolved in it may not pass so easily. A weak solution may cause the flow of water from it to the stronger solution. This mechanism is more significant for drawing in chlorides and sulfates to the concrete sample.

Concrete is generally regarded as a durable material but due to its versatility for many situations, it can be vulnerable to attack from a variety of exposures. Kumar and Bhattacharjee (*2003*) stated that the durability of concrete is predominantly dependent on its permeation properties. Both the transport properties and the durability of concrete are affected by the permeable porosity (*Safiuddin & Hearn, 2005*). A comparable study of ASTM saturation techniques by Safiuddin & Hearn concluded that permeable porosity of concrete decreases with increasing curing age and vacuum saturation is the most effective ASTM saturation technique (*Safiuddin & Hearn, 2005*).

The permeation can be classified as low, average or high by determining a permeation index by a number of tests including the initial surface absorption test (ISAT) (*Bungey, 1989*), in accordance with BS 1881-208:1996, or water absorption of drilled cores (*Campbell & Roper, 1996)*. ISAT has been successfully used and is the most common test to assess the durability of concrete (*Kumar and Bhattacharjee, 2002*) in respect of the initial surface absorption. The tests record the ingress of fluids into concrete that is influenced by transportation within the pore structure (*Garboczi, 1990*) and these fluids result in chemical and physical changes leading to the deterioration of the concretes structure. Garboczi (*1990*) state that the deterioration of the concrete itself is not considered by the permeation tests just the means by which media travels

through the structure. The rate of deterioration, and its extent, is largely due to the pore structure that is indicative of the pore size distribution (*Garboczi, 1990*) and the transport mechanism; absorption, diffusion or permeability.

The concrete structure contains cement paste and aggregates that influence the pore size and distribution during and following hydration. The diversity of pores within the cement paste alone is indicated in Figure 2.8. In addition to these found in the cement paste pores can be found elsewhere within the concrete. Aligizaki (*2006*) divides the pores found in concrete into five classes;

1. Cement paste matrix pores (including gel pores, capillary pores, hollow-shell pores and air voids)
2. Pores in aggregates
3. Pores associated with the interface between aggregates and cement paste
4. Water voids such as those created by water bleeding and construction
5. Internal discontinuities in the cement paste such as those caused by humidity and temperature changes

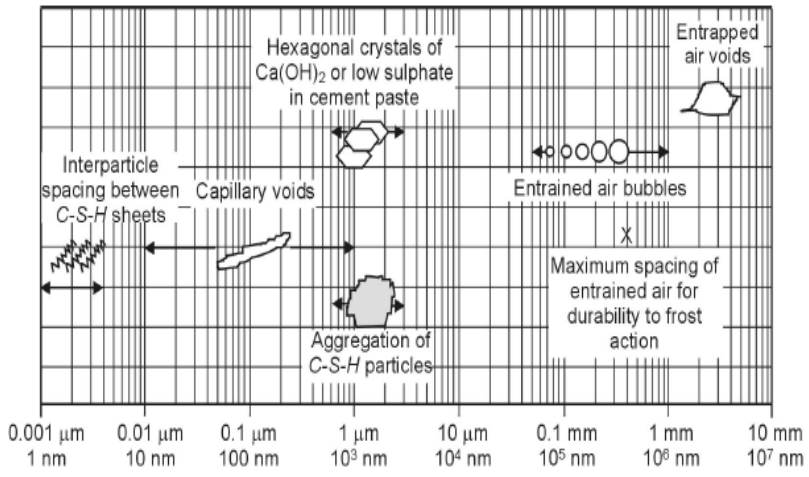


Figure 2.8: Dimensional rage of solids and pores in hydrated cement paste

(Source: A. M. Neville 1995)

The volume, size and continuity of pores are influential on the permeation and strength of concrete (*Basheer et al, 2005*) with macro pores of sizes larger than 50µm being the most detrimental to both strength and impermeability (*Mehta & Monterio, 1993*). Basheer et al (*2005*) studied the effects of different sizes, or grades, of coarse aggregate. After obtaining an average aggregate size from sieve analysis the concrete was cast and air permeability tests carried out. The results, summarised in Figure 2.9, showed that as the average size of aggregate increased the air permeability index also increased suggesting that durability could be improved by lowering the average size of combined fine and coarse aggregates. In addition to air permeability, Basheer et al (*2005*) tested salt scaling and carbonation. The results of the latter also showed that carbonation increased when the aggregate size was increased, believed to be due to an increase in the porosity and size of the ITZ around the coarse aggregate.

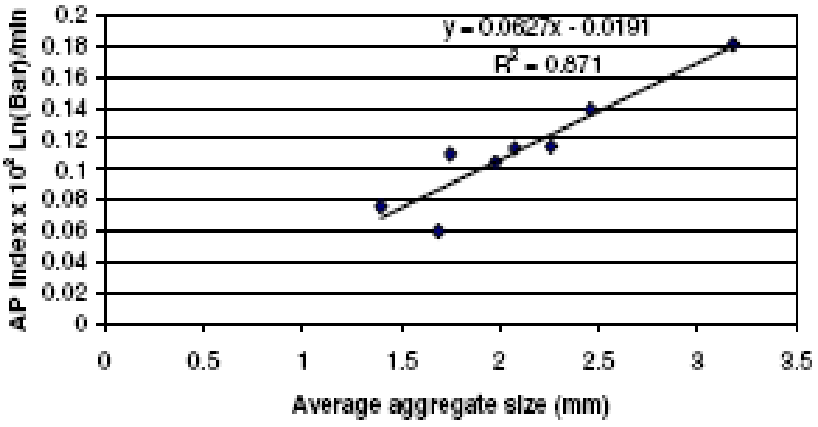


Fig 2.9: Effect of average aggregate size on air permeability index

(Source: Basheer et al, 2005)

Carbonation

Carbonation, the reaction of CO_2 with hydrated cement, occurs naturally and progressively from the outside exposed surface of concrete. CO_2 is present in the atmosphere (in rural areas this can be approximately 0.03% by volume, increasing to 0.3% in cities) and diffuses through the pore spaces to react with the hydration products within the cement system. The volume of $Ca(OH)_2$, calcium hydroxide, formed by the hydration of CEM I will affect

the rate of carbonation as it is the most reactive with CO_2 which turns to carbonic acid in the presence of moisture. The process is shown by the following equation:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

[Eq 2.7]

According to Mehta & Monteiro the calcium carbonate precipitated in this reaction is insoluble and will stop unless free CO_2 is present in the water when a further reaction will occur, producing soluble bicarbonate.

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

[Eq 2.8]

This reaction itself, is reversible and requires a certain amount of free CO_2 (balancing CO_2) which is required to maintain the equilibrium (*Mehta & Monteiro, 2006*). The rate of hydration, given the previous discussion, is dependent on the permeability of the concrete, moisture content, CO_2 content and relative humidity. Whilst Neville states that it does not cause deterioration of the concrete directly it does have fundamental effects on its overall durability (*Neville, 1995).* Sisomphon & Franke (*2007*) found that in the case of carbonation the rate declines with age using an accelerated carbonation test. Any cracks in concrete will undoubtedly increase the rate of carbonation (*Detweiler et al, 1996*) as the exposed surface area is greater and further increased if the relative humidity of the atmosphere is 50% (*Mindess & Young, 1981*).

The process of carbonation affecting binary concretes is more complex. There is a lower volume of $Ca(OH)_2$ in binary concretes containing GGBS and it is more likely to be completely carbonated. Once this occurs carbonation will take place within the CSH. As discussed previously the volume of CSH in binary concretes, GGBS or fly ash, is greater because of this carbonation will be exacerbated due to the high levels of $CaCO_3$. Sisomphon & Franke studied GGBS together with Portland cement and fly ash concrete following 3, 7 and 28 day water curing. The GGBS cement showed increased carbonation compared to the Portland

cement control, after 7 and 28 days curing and the GGBS was better than the 50% fly ash addition. This confirms Osborne's earlier study of carbonation of GGBS concretes in 1986, which concluded that poorly cured concrete can exhibit very high carbonation with high slag contents increasing carbonation further (*Horiguchi et al, 1994*). Chang & Chen (*2006*) use varying methods to determine carbonation and evaluate its purpose together with thermogravimetric analysis (TGA), XRD and pore solution tests. By examining a number of different methods Chang & Chen determined that there were three distinct regions of fully carbonated, partially carbonated and non-carbonated zones within the concrete structure (*Chang & Chen, 2006*). Only CEM I concrete was tested so the effects of additional material remain to be examined in this detail.

Chloride

Concretes are used globally in many different environments that can include exposure to chloride. Whilst chloride does not directly affect the concrete itself, it does cause corrosion of steel reinforcements if the surrounding concrete is damaged or permeable. This can be directly through sea water in marine environments or even near to marine sources transported by wind (*Neville, 1995*). Whilst concretes used for marine environments are designed specifically with this in mind, effects of de-icing agents in other environments also represent a risk.

The method by which chloride ions are transported into concrete is complicated, involving the previously discussed diffusion; permeation and capillary suction (*Kropp & Hilsdorf, 1995*). In addition convective flow through the pore system and network of micro-cracks within the concrete matrix also need to be considered and will depend on the exposure conditions, as summarised in Table 2.7.

In addition to these transport mechanisms interaction between the chloride ions and cement occurs by which they can be chemically bound onto pore walls (*McCarthy, 1991; Nokken et al, 2003*). It is chloride binding that Glass & Buenfeld state may affect not only the rate of chloride ingress, but the threshold level (*Glass & Buenfeld, 2000*). The tricalcium aluminate (C_3A) content of cement is the dominant factor affecting chloride binding, increasing binding with increasing C_3A volume (*Glass & Buenfeld, 2000; Papdakis & Tsimas, 2002*). The C_3A

reacts to produce calcium chloroaluminate, a compound that contains chloride in a chemically bound form, often referred to as Freidel's salts:

$$3CaO \cdot Al_2 \cdot O_3 \cdot CaCl_2 \cdot 10H_2O \leftrightarrow 4Ca^{2+} + 2Al(OH)_4 + 2Cl + 4OH + 4H_2O$$

[Eq 2.9]

Table 2.7: Summary of primary transport mechanism for exposure and structure type (CCA, 2009)

Exposure	Example of structure	Primary Transport Mechanism
Submerged	Basement exterior walls or transport tunnel liners below low tide. Liquid containing structures.	Permeation/Diffusion/ Wicking Action
	Substructures below tide.	Diffusion
Tidal	Substructures and superstructures in the tidal zone.	Capillary Absorption Diffusion
Splash & Spray	Superstructures about high tide in the open sea.	Capillary Absorption Diffusion
Coastal	Land based structures in coastal areas or superstructures above high tide river estuary or body of water in coastal areas.	Capillary Absorption

Whilst it is evident that the C_3A content of the cement is an affecting factor, Glass & Buenfeld also state that GGBS can also affect the rate of binding of chlorides, as too does fly ash (*Glass & Buenfeld, 2000*), increasing binding capacity at certain hydroxyl concentration (*Glass et al, 1997*). The effectiveness of both GGBS and fly ash as binary constituents in chloride binding is shown in a number of studies.

Sivasundaram & Malhotra (*1992*) state that GGBS concretes show good resistance to chloride penetration. Mejia et al (*2003*) tested a number of binary mixes with different pozzolanas and GGBS Figure 2.8 shows that GGBS replacement of 70% [OPC1 +S(70%) in Fig 2.10] gave improved chloride concentration compared to the Portland cement control (OPC1) and binary mixes incorporating fly ash (FA), natural pozzolans (NP) and silica fume (SF) (*Mejia et al, 2003*). McPolin et al (2005) showed more clearly an improved rate of chloride ingress in Figure 2.11 at a 50% GGBS level. These improvements are due to the increased binding of

chloride due to the additional calcium aluminate hydrates in the reaction and a resulting, denser matrix (*Oh et al, 2002*). In addition the GGBS leads to higher volumes of Freidal's salts due to higher aluminate levels (*Dhir et al, 1996*)

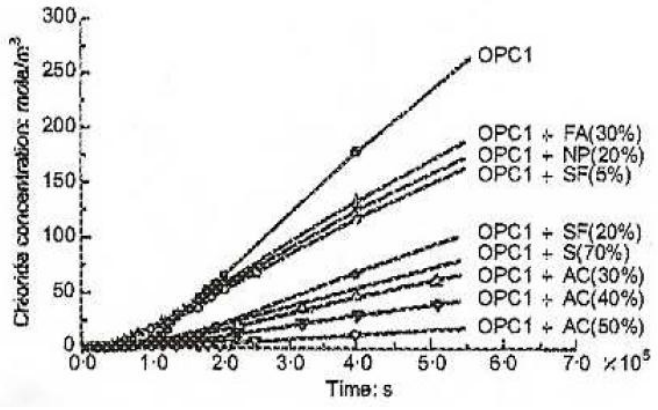


Fig 2.10: Variation of chloride concentration with time from Mejia et al, 2003.

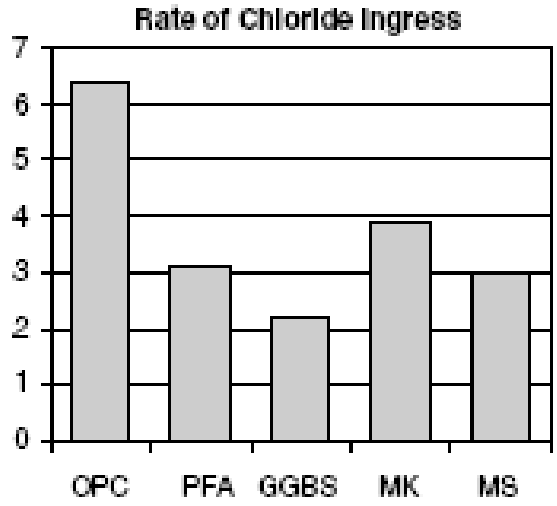


Fig 2.11: Rate of chloride ingress from McPolin et al, 2005

2.7 Ternary Blended Concretes and Their Properties

Due to the limited number of papers on ternary blends, additional materials such as silica fume and metakaolin have also been briefly covered in this review. This enables detailed coverage of ternary blended cements that have been studied to date to be made.

2.7.1 Fresh Properties

Unlike binary concrete there is limited information on the fresh properties of ternary cement concretes, although the fluidity would be expected to change due to the properties of the additions used. Thomas et al (*1999*) studied ternary blends incorporating Portland cement, silica fume and a range of different fly ashes. The study concluded that fly ash compensated for some of the workability problems usually associated with silica fume when used at high levels. Li & Zhao (*2003*) studied the addition of different levels of superplasticisers added to a concrete of water/binder ratio 0.28 to achieve equal workability. 1.7% by mass of the water/binder ratio was required for the 100% Portland cement mix, 1.5% for the 40% fly ash binary mix and 2.0% for the ternary mix incorporating 25% fly ash and 15% GGBS thus indicating that the fluidity is affected by the additional materials. Elahi et al (*2010*) included ternary blends of Portland cement, GGBS and silica fume as well as Portland cement, fly ash and silica fume. A water/cement ratio of 0.3 was used as per Li & Zhao's study and the superplasticiser was adjusted accordingly, again to achieve equal workability. For the GGBS ternary blend this was 2.5% by mass and greater than the fly ash ternary blend (*Elahi et al, 2010*).

Nehdi et al (*2004*) studied a ternary blend of CEM I, fly ash and GGBS as well as quarternary mixes incorporating silica fume and rice husk ash (RHA). All mixes had a constant water/cement ratio of 0.38. The measured density of the ternary mix equalled the CEM I, whilst the slump increased by 30mm, by using a viscosity-modifying admixture (VMA) the slump was reduced from 690 to 615mm when combined with a high range water reducer compared with the control mix. Nehdi et al (*2004*) found that the SP dosage for mixes incorporating 50% replacement of CEM I was lower unless the VMA or the RHA was added.

2.7.2 Strength Development

Thomas et al (*1999*) tested both the compressive strength and diffusion of water through the concrete microstructure and refer to the results as showing "synergistic effects"; as shown in Figure 2.12. The silica fume in the mixes tested by Thomas et al (*1999*) compensated for the relatively low early strength of fly ash concretes. In addition to the fly ash increasing the long term strength development of silica fume concrete, it also offset the increased water demand of silica fume and the increased cost. The effects of fly ash and silica fume ternary blends on chloride diffusivity were also apparent with a very high resistance to chloride ion penetration.

Shehata & Thomas (*2006*) carried out further studies following their earlier work, specifically investigating the suppression of alkali-silica reaction by using ternary blends of silica fume and fly ash. In this instance, both high and low alkali cements were combined with high silica and low alkali content silica fume and 3 types of fly ash with low, moderate and high calcium oxide content. Shehata & Thomas (*2006*) concluded that silica fume and fly ash introduced to high alkali CEM I systems were effective in reducing the expansion due to ASR to levels of <0.04% after 3 years.

Antiohos et al (*2007*) studied ternary blends based on fly ash systems, with each combination consisting of PC and 2 types of fly ash. Antiohos et al (*2007*) found that the beneficial assets of one fly ash can compensate for the other and blending them therefore resulted in improvements in mechanical properties when compared to the respective binary system. It was found the ratio of 50:50 with the two fly ashes were most effective, and as there was no significant alteration in the nature of the hydration the performance was attributed to synergistic effects.

Li & Zhao (*2003*) undertook a comparative study of 3 mixes; PC control (PCC), high volume fly ash with high strength cement (HFAC) and fly ash with GGBS (GGFAC). Short-term and long-term performance tests on the compressive strength were carried out and resistance to sulphuric acid (H_2SO_4). It was evident that that the GGFAC blend was able to achieve an adequate early age compressive strength and maintain long-term strength, higher than the PC

Control (Figure 2.13). It was also clear that the GGFAC blend was superior to both other mixes against sulphuric acid attack, with a weight change of about 8% after 50 weeks exposure to 2% H_2SO_4 solution (Figure 2.14)

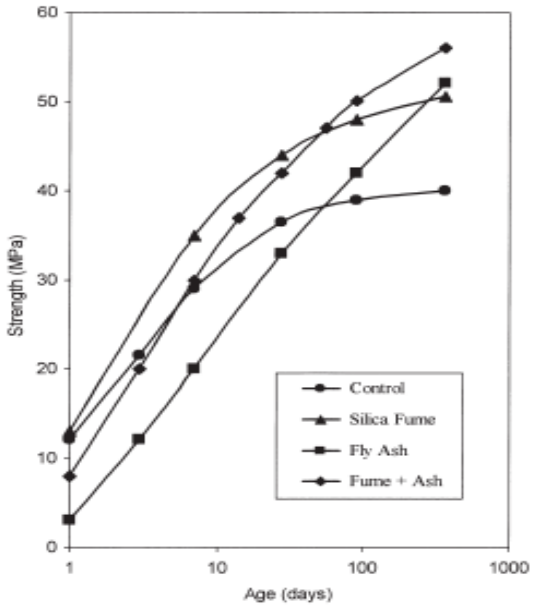


Fig 2.12: Compressive strength development in concrete effect of silica fume and low lime fly ash. (Thomas et al, 1999)

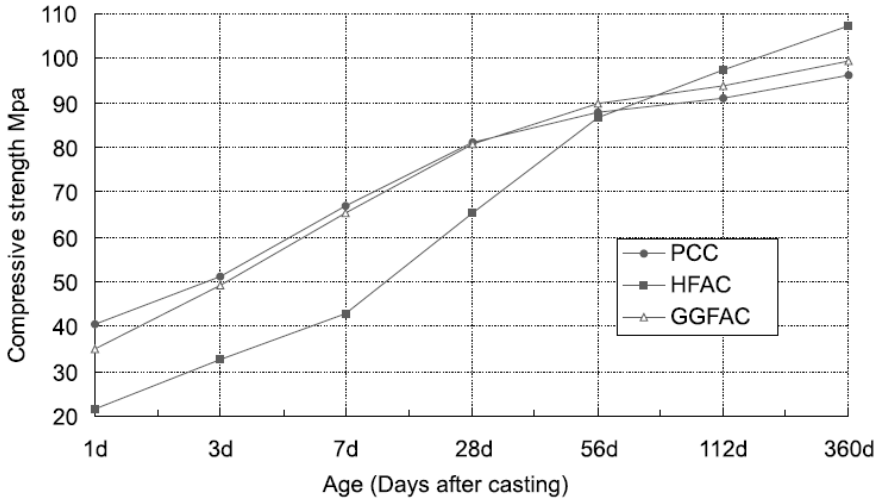


Fig 2.13: Development of the compressive strength versus time. (Li & Zhao, 2003)

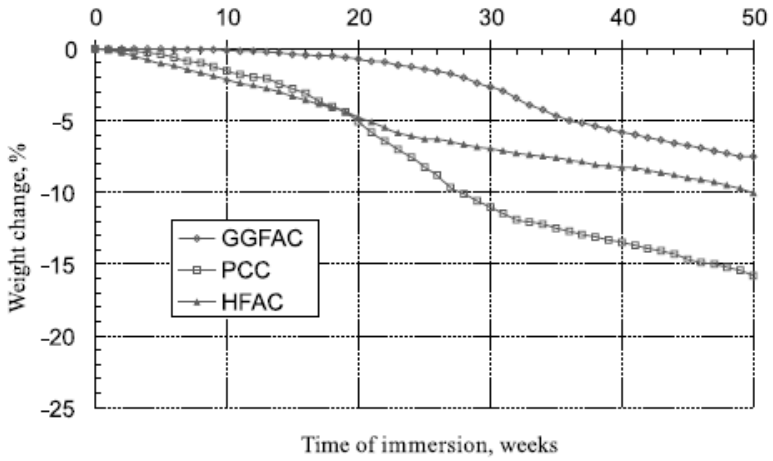


Fig 2.14: Weight change of concentration in 2% H_2SO_4 solution.

(Li & Zhao, 2003)

Laldji & Tagnit-Hamou (*2006*) incorporated alternative supplementary cementitous material (as they are referred to in America). Glass frit, an engineered material made from recycled spent pot liners from aluminium production, was blended with PC and silica fume to produce a ternary blend and fly ash and GGBS were added to produce two quaternary blends. At an early age the compressive strength of the concrete containing the glass frit was lower than the control, but at 28 and 91 days there was a marked improvement of between 2 to 10 N/mm^2. Khatib & Hibbert (*2005*) used ternary blends of PC, GGBS and Metakaolin at different proportions. Metakaolin was incorporated at two levels, 10% and 20% to produce the mix combinations shown in Table 2.8.

Tests for compressive strength and E-value found that incorporating up to 60% GGBS in concrete caused both an increase in long-term compressive strength and E-value, shown in Figure 2.15. Additionally an increase in metakaolin content in concrete up to 20% increased strength at early ages. This increase in early age strength does not normally occur before 28 days when only GGBS is used (*Khatib & Hibbert, 2005*).

Table 2.8: Mix proportions use by Khatib & Hibbert (2005)

PC	GGBS	MK
100%	-	-
90%	-	10%
60%	30%	10%
40%	50%	10%
20%	70%	10%
80%	-	20%
60%	20%	20%
40%	40%	20%
20%	60%	20%

Nehdi et al (*2004*) found that a ternary blend incorporating 25% GGBS and 25% fly ash improved the early age compressive strength when compared to the binary fly ash mix and quarternary mixes with 20% GGBS and 6% RHA or silica fume. The 28 day strength exceeded the CEM I (100% OPC) mix. Both ternary mixes either with or without VMA (viscosity modifying admixture) give almost identical results as shown in Figure 2.16 (*Nehdi et al 2004*).

More recently Elahi et al (*2010*) studied the mechanical and durability properties of concrete containing GGBS and silica fume. As is clear in Figure 2.17, (*Elahi et al 2010*), the binary mixes containing 50% and 70% GGBS gave lower results than the ternary mix incorporating silica fume, which at 28 days was the only mix out of the three that exceeded the CEM I control. Interestingly, neither of the binary mixes exceeds the strength of CEM I at any age, contradicting the effects of GGBS documented in other studies.

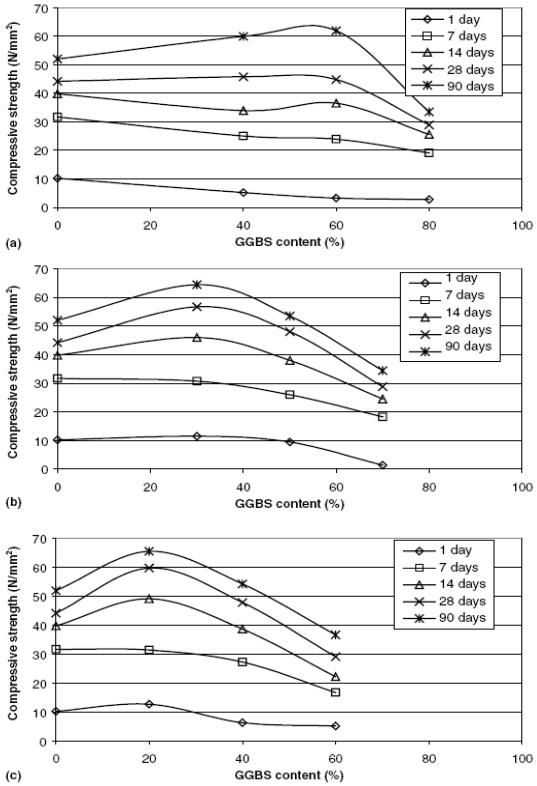


Fig 2.15: Influences of varying GGBS contents at

(a) 0% MK, (b) 10% MK and (c) 20% MK.

(Khatib & Hibbert, 2005)

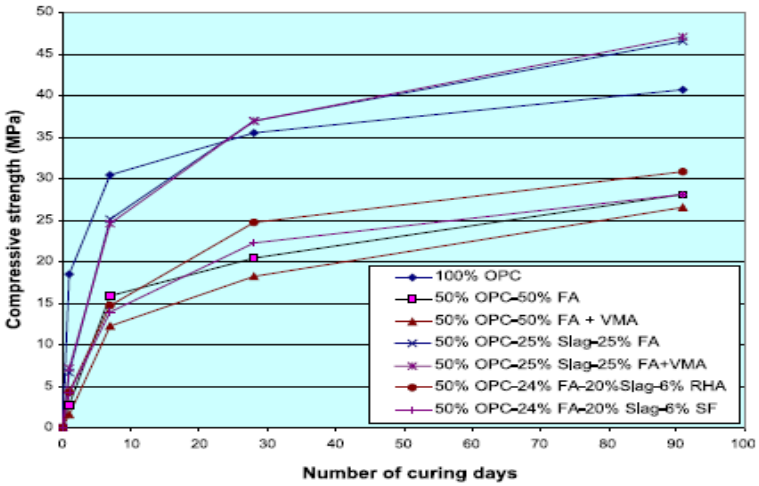


Fig 2.16: Compressive strength versus time for the SCC mixes tested by Nehdi et al

(Nehdi et al, 2004)

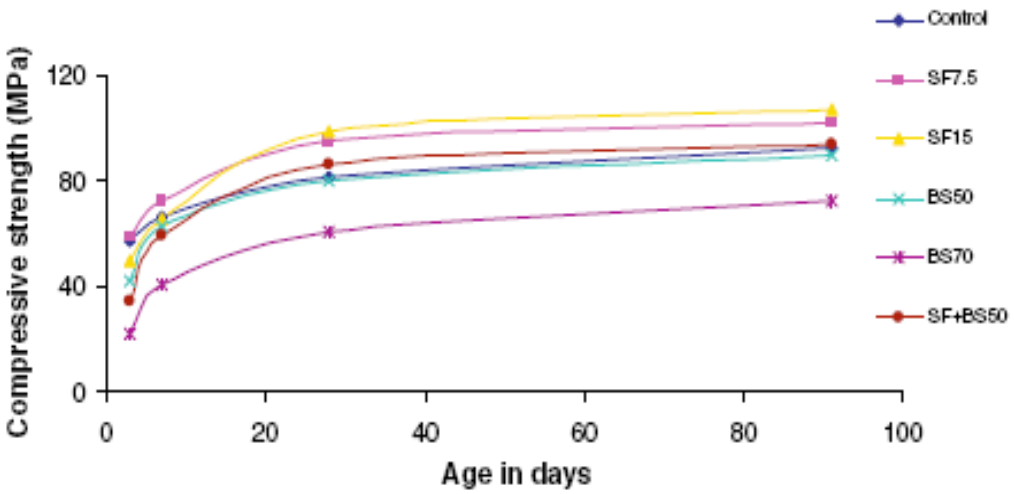


Fig 2.17: Compressive strength development of binary and ternary mixes containing silica fume and GGBS (Elahi et al, 2010)

2.7.3 Durability

As already noted there are limited papers concerned with ternary blend cements. Those that exist, in the main cover CEM I, fly ash plus an addition other than and GGBS (for example, metakaolin or silica fume). Those that do cover CEM I and GGBS are more concerned with durability of these types of concrete, more specifically resistance to chloride attack. The limited studies using ternary blends incorporating silica fume are reviewed briefly.

Permeability

Alexander & Magee (*1999*) carried out oxygen permeability index (OPI) and a water sorptivity test, the results of which are given in Table 2.9. The OPI of the ternary blends ranged from 9.62 to 10.00 depending on the water/binder ratios, with that of 0.49 producing excellent performance *(Alexander & Magee, 1999)*. These were out performed by both the control mix and binary silica fume mixes. The excellent performance of the ternary mixes was repeated also in water sorptivity tests. The ternary mixes produced lower index values than those of the control tests.

Table 2.9: Durability index tests obtained from wet cured test specimens, Alexander & Magee, 1999)

Durability index test results obtained for wet-cured test specimens

	Estimate of concrete performance [9]			
Index test	Excellent	Good	Poor	Very poor
Oxygen permeability index range	>10.0	9.5–10.0	9.0–9.5	<9.0
Water sorptivity range (mm/√h)	<6.0	6.0–10.0	10.0–15.0	>15.0
Chloride conductivity range (mS/cm)	<0.75	0.75–1.5	1.5–2.5	>2.5

	Durability index test results		
Binder combination	Oxygen permeability index	Water sorptivity (mm/√h)	Chloride conductivity (mS/cm)
(1) Water/binder ratio = 0.66			
PC control	9.71	7.60	2.22
PC/50% GGBS	9.25	6.24	2.15
PC/5% CSF	10.03	5.71	1.22
PC/10% CSF	10.19	4.84	0.91
PC + 10% CSF (w/b = 0.60)	10.30	3.95	0.63
PC/40% GGBS/10% CSF	9.62	5.00	0.52
(2) Water/binder ratio = 0.56			
PC control	9.97	7.08	1.93
PC/50% GGBS	9.56	5.85	0.81
PC/5% CSF	10.28	5.10	0.95
PC/10% CSF	10.42	4.27	0.68
PC + 10% CSF (w/b = 0.50)	10.34	3.42	0.50
PC/40% GGBS/10% CSF	9.87	4.41	0.36
(3) Water/binder ratio = 0.49			
PC control	10.03	5.58	1.49
PC/50% GGBS	9.69	5.07	0.63
PC/5% CSF	10.36	4.45	0.81
PC/10% CSF	10.43	4.13	0.62
PC + 10% CSF (w/b = 0.44)	10.34	3.44	0.48
PC/40% GGBS/10% CSF	10.00	4.15	0.31

Ganjian & Pouya (*2008*) used a water absorption test in accordance with RILEM-CPC-11.2 “Absorption of water by concrete by capillarity” to examine the effects of the Persian Gulf tidal zone on paste and concrete samples. They compared binary silica fume mixes with a ternary mix consisting of 40% PC, 10% silica fume and 50% GGBS in three different exposure conditions - potable water, simulation tank and site tidal zone. The simulation tank used a synthetic seawater solution with cyclic wetting and drying, the conditions were stated by Ganjian & Pouya to be harsher and more severe than the normal conditions at the site tidal zone. The results for both the paste and concrete specimens are summarised in Figures 2.18 and 2.19, respectively. It was concluded from this work that the use of silica fume in the cement combination for tidal marine structures in the Persian Gulf was detrimental *(Ganjian & Pouya, 2008)*. The use of GGBS to produce a ternary mix increased the absorption factor in both the simulated and tidal zone exposures. Again Elahi et al (*2010*) studied ternary blends incorporating silica fume with GGBS. With the inclusion of 7.5 % silica fume, the air permeability, which Elahi et al tested at 44 days, was reduced compared to the binary mix. At

the later 91 day test the air permeability increased. Elahi et al (*2010*) suggest this difference to be a result of micro-structural change and that the influence of tortuosity and interfacial transition zone is different between air permeability and sorptivity tests as they measure two different physical characteristics of the pore structure. The sorptivity tests carried out by Elahi et al (*2010*) showed a significant decrease at both test ages with the addition of 7.5% silica fume.

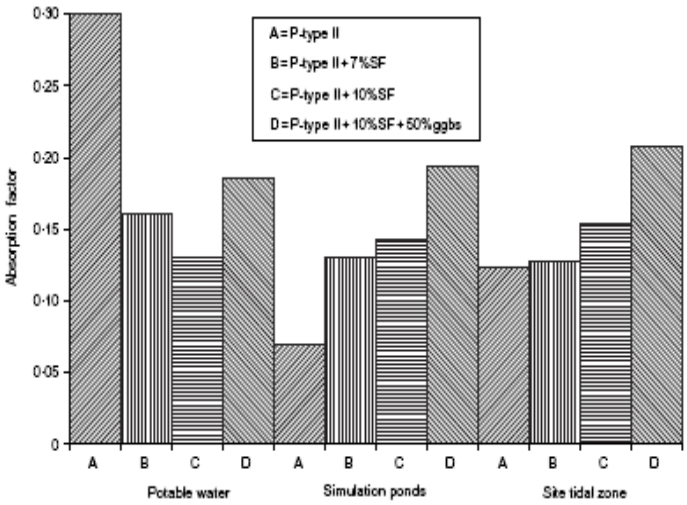


Fig 2.18: Absorption factors for pastes exposed to different conditions (Ganjian & Pouya, 2008)

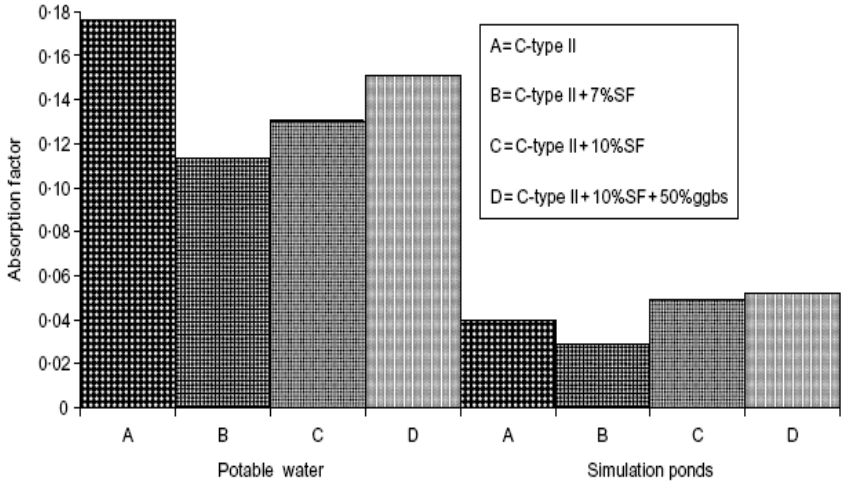


Fig 2.19: Absorption factors for concretes exposed to different conditions (Ganjian & Pouya, 2008)

Carbonation

The process of carbonation was discussed earlier in relation to binary concretes, it would be further complicated with an additional ternary material. It is possible that a ternary material may reduce the rate of carbonation by improving the concrete's resistance to permeability, or exacerbate it further. Sisomphon & Franke (*2009*) studied accelerated carbonation rates of blast-furnace slag concrete (CEM III-B) combined with 50% fly ash and their results are shown in Figure 2.20 where it is clearly illustrated that the addition of fly ash with a slag concrete significantly increased the depth of carbonation, leading to the recommendation of a cover thickness of 35 to 40mm for reinforced concrete made with this combination. The results of depth of carbonation were estimated based on accelerated carbonation depths. Sisomphon & Franke (*2009*) suggested that the high depth of carbonation is due to lower portlandite content ultimately resulting in a lower level of CO_2 binding. The carbonation occurs with the CSH in the ternary concretes once the Ca(OH)2, which is lower in volume, is completely carbonated. The consequence of this is the creation of pores greater than 100nm that aid carbonation further together with the reduced pH of the pore water from around 13 to 8.3 (*Papadakis et al, 1991*).

Chloride Ingress

The transportation mechanism of chlorides and the process of binding were discussed previously, in relation to the ability of GGBS and, indeed, fly ash to ingress the rate of chloride binding. Chloride tests seem to be one of the most widely covered areas within the literature, with ternary combinations tending to focus on the effects of silica fume.

Alexander & Magee (*1999*) used a conductivity method to determine this property (Table 2.9) and found that ternary blends consisting of PC, GGBS and silica fume achieved optimum performance at all three water/cement ratios tested, when compared to binary blended cements. Sharfuddin et al (*2008*) used a similar test on ternary mixes of PC, GGBS and silica fume and found that they produced a lower charge when compared to the respective binary mixes.

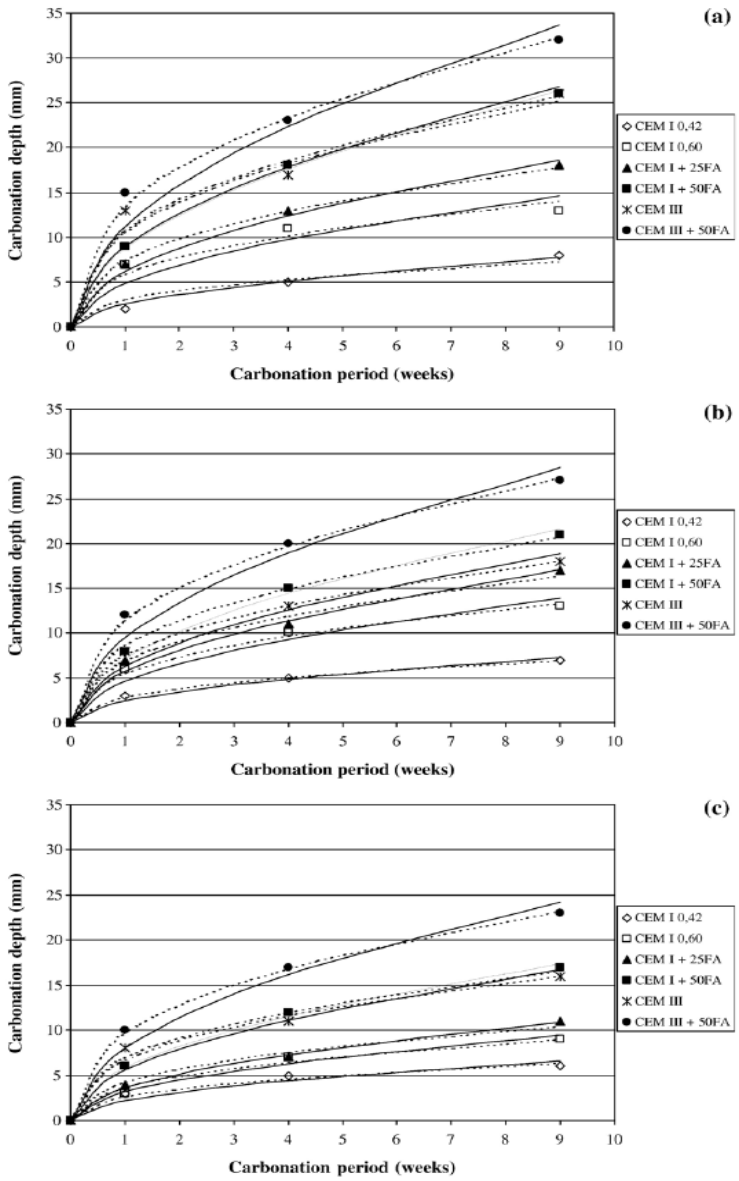


Fig 2.20: Relationship between the best fit of carbonation depth and the linear exposure time (a) 3 day (b) 7 day (c) 28 day curing. (Sisomphon & Franke, 2009)

Hooton & Titherington (*2004*) examined the effects of two curing techniques, ambient and accelerated, on chloride resistance of ternary cement concrete using three different chloride tests including the Rapid Chloride Penetration Test (RCPT), migration and bulk diffusion. Hooton & Titherington (*2004*) tested ternary blends consisting of CEM I, GGBS and

silica fume. These performed well with 'superior chloride penetration resistance' *(Hooton & Titherington, 2004)*. These authors also found that ternary blends had the advantage of being easier to place and finish. Becknell & Hale (*2005*), using the RCPT however, found that ternary blends did not follow 'expected trends', their results are shown in Figure 2.21. The charge passing increased when fly ash was added to the 20% GGBS mixes, but the opposite occurred when GGBS was added to the 20% fly ash mixes and continued to decrease as the volume of GGBS increased. Becknell & Hale (*2005*) suggested that, with the presence of pozzolanic materials, the ASTM test results can be 'skewed' as this presence can change the chemical composition of the concrete pore solution. Sharfuddin et al (*2008*) found that the RCPT test proved to be more sensitive in showing appreciable differences between the mixes. Supporting Nehdi et al's study in 2004 that included a ternary mix of 25% GGBS and 25% fly ash, they found that this particular mix reduced chloride ion penetrability. All of the GGBS (slag) mixes were improved as shown in Figure 2.22 below.

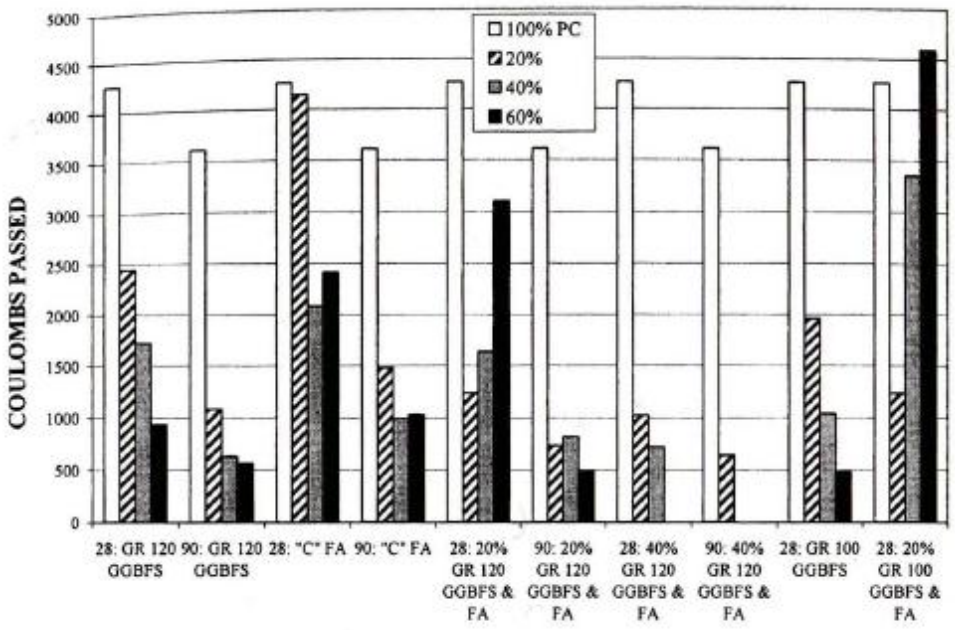


Fig 2.21: RCPT test results from Becknell & Hale.

(Becknell & Hale, 2005)

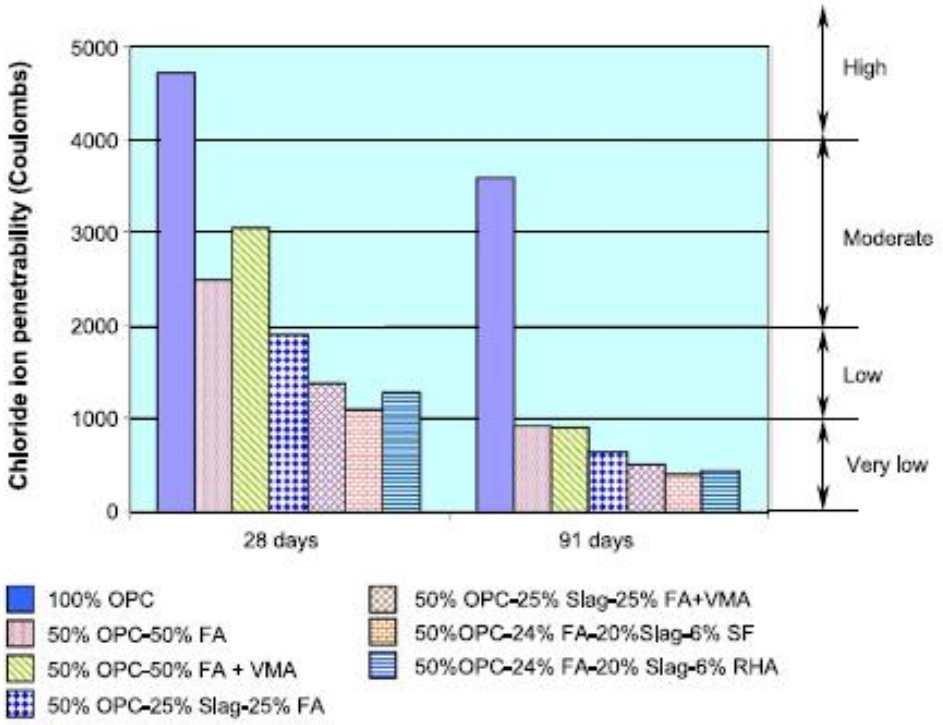


Fig 2.22: Chloride ion penetrability at 28 & 98 days for the mixes tested by Nehdi et al (2004)

Bleszynski et al (*2002*) carried out work to compare laboratory and field study conditions. Outdoor exposure sites in Canada were considered ideal due to their heavy traffic and frequency of de-icing salt application. They were also suitable for freeze-thaw studies due to the numerous cycles per year. Bleszynski et al (*2002*) concluded that ternary blends provided the 'least penetrable concrete' during the RCPT as indicated in Fig 2.23. The ternary blend of 5.2% silica fume and 25% GGBS yielded the best results, which were comparable to Hooton & Titherington's tests on ternary blends of 8% silica fume and 35% GGBS that gave 175 and 125 coulombs for ambient and accelerated curing respectively. This is further supported by Elahi et al's (*2010*) more recent study, which found that the ternary mixes comprising of 7.5% silica fume were better for resisting chloride ions (*Elahi et al, 2010*). Further comparisons between Hooton & Titherington (see Figure 2.24) and Bleszynski et al (*2002*) can be drawn from the bulk diffusion tests that both studies carried out. Again both papers indicate that ternary blends achieved greater resistance *(Bleszynski et al, 2002)*.

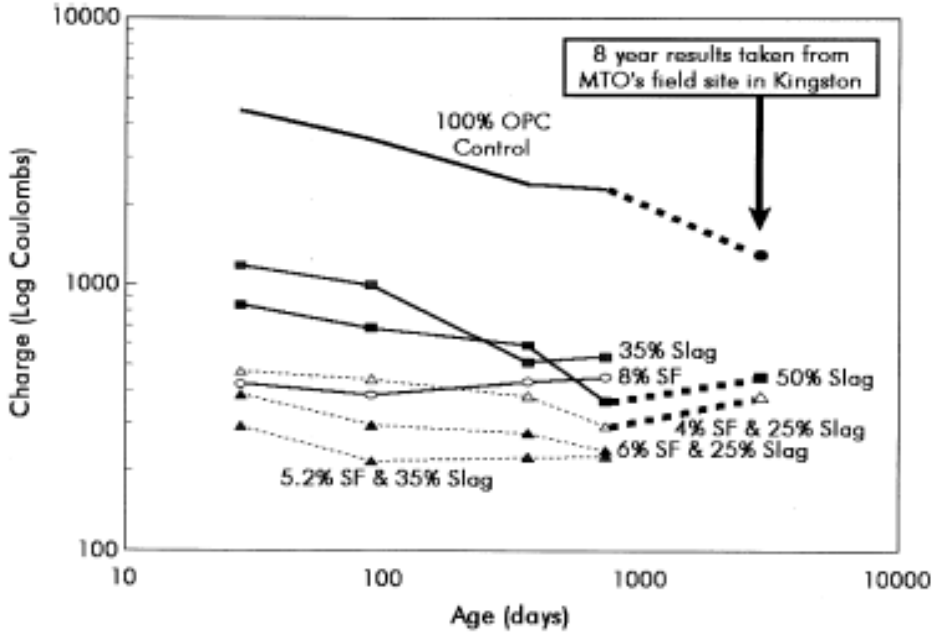


Fig 2.23: Bleszynski et al RCPT tests indicating the lower levels of chloride ingress for Slag cements (Bleszynski et al, 2002)

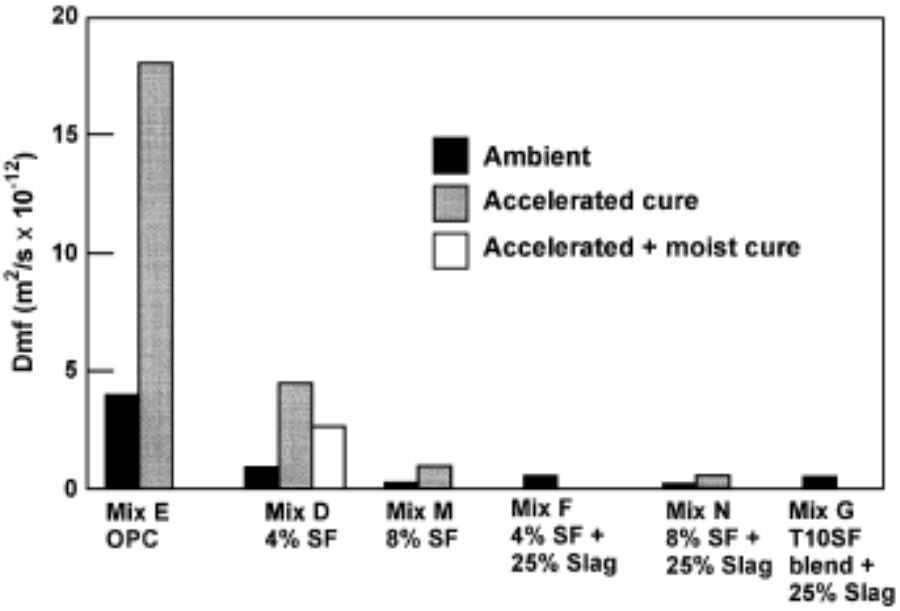


Fig 2.24: Effect of cementing materials and curing on steady state migration (Hooton & Titherington, 2004)

Long (*2005*) used a Rapid Chloride Migration method (RCM) with a seven day test duration, following pre-conditioning of both 28 and 91 days, ending in a the specimen cylinder being split longitudinally and sprayed with an indicator solution to determine the depth of penetration. Results from this test are shown in Figure 2.25. Whilst the results indicate that the chloride migration coefficient was lower for the ternary mixes they were still not as low as the binary slag mixes.

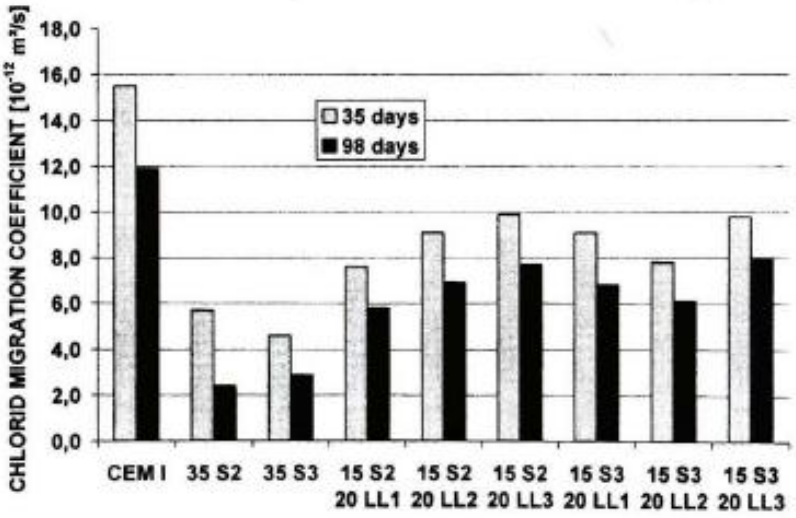


Fig 2.25: Chloride migration in concretes made with 320kg cement/m³, w/c 0.50. (Long, 2005)

2.8 Embodied CO_2

It cannot be disputed that the current issues surrounding climate change have resulted in increasing pressure on the industry to a commit to sustainable development. The fact that the cement industry is a significant contributor in the emission of CO_2, as discussed in the previous chapter, necessitates the consideration of the impact of concrete production from cradle to grave. Essentially the embodied CO_2 of concrete is fast becoming an issue for the industry, given the importance of this and its effect on the future of sustainable development life cycle analysis of concrete is becoming a widely discussed issue.

For the concrete industry there are a number of issues to be addressed with regard to its impact on the environment throughout all stages of its life cycle. Not only are there issues concerning natural resource use in the raw materials required to produce cement and the

aggregates needed for the concrete but cement production alone accounts for 5% of global anthropogenic CO_2 emissions (*Hendricks, 2005*) of this 50% is from the combustion process and 50% from the calcinations process. The production process itself releases 0.5 tonne of CO_2 for every tonne of CaO produced as part of the chemical reaction, whilst approximately 0.43 tonnes is produced by the manufacturing process:

$$CaCO_3 \rightarrow CaO + CO_2$$

[Eq 2.8]

This decomposition of limestone is an essential part of the cement production and occurs within the kiln which also consumes high levels of energy thus creating CO_2 emissions. 2% of global primary energy consumption is used in cement production (*WEC, 1995*). In spite of this Hendricks (*2005*) states that options exist for reducing such an impact. The use of more energy efficient processes and replacing high with low carbon fuels are considered. In most countries rotary kilns are used but shaft kilns are more common in developing countries, where production rates continue to rise, to a greater extent. Regardless of the method it is an energy intensive process with 1.75 ± 0.1 MJ required for each kilogram of clinker produced (*Hendricks, 2005*) and the clinker to cement ratio varies from 0.5 to 0.95 for Portland cement thus effecting the CO_2 emissions. Hendricks also suggests, in addition to lower clinker/cement ratios, alternative cements can be used to reduce environmental impacts. The use of cement combinations depends very much on current application levels, availability, standards and legislation.

The total ECO_2 for the production of cement alone is in the region of 930kg per tonne of Portland cement produced in the UK (*BCA, 2008*). Other studies have reported ECO_2 from 80% to 100% (*Flower & Sanjayan, 2007*), 83% was reported by Hendricks in 2005 based on Australian figures. For the purposes of this study the ECO_2 for each mix combination was calculated based on the BCA figures that for every tonne of cement produced 930kg of ECO_2 is emitted and that for every tonne of GGBS and fly ash 52 kg and 4kg of ECO_2 are emitted respectively. Flower & Sanjayan (*2007*) reported the ECO_2 of fly ash to be 0.027 t CO_2 –e/tonne effectively 3%, or 3kg per tonne of fly ash produced, so there is little difference between their study and the BCA figures. However, Flower & Sanjayan stated that the emission factor of

GGBS is 0.143 t CO_2 –e/tonne, 14% or 14kg of GGBS produced. Their study was based on audits undertaken in Australia where there may be differences in processing.

The emission figures are based purely on the processing of materials subsequent to their initial production as both GGBS and fly ash are by-products of other industrial processes that operate independently of the cement industry and would therefore be produced regardless of their beneficial characteristics as cement additions. Use of these materials in cement production has the added benefit of reducing waste to landfill in addition to ECO_2 per tonne of concrete produced. In order to calculate more accurately the ECO_2 of the mix combinations other components should also be considered. The ECO_2 of cement has already been discussed and given the amount required to produce 1 tonne of concrete the ECO_2 it is high when compared to that of the sand and aggregates. The production process of sand and fine aggregates involves hauling, washing and grading requiring equal amounts of diesel and electricity. Flower & Sanjayan (*2007*) report on audit findings for one quarry in Australia where the ECO_2 is said to be in the region of 0.0139 t CO_2 –e/tonne and includes the subsequent transportation of the sand to the mixing site.

The production process of coarse or crushed aggregate is generally 30-40% higher in emissions than that of sand depending on the type of aggregates being used. The process itself begins with blasting from quarry faces into medium sized rocks before excavating and hauling to crushing and grading equipment. Flower & Sanjayan report the ECO_2 for basalt to be 0.046 t CO_2 –e/tonne. The process also requires on average 22% diesel and 78% electricity, the latter of which is used extensively for the crushing stage which itself accounts for 75% of the total process. The Concrete Industry Sustainability Performance Report, published in 2010, indicated the CO_2 emissions per tonne of aggregate produced to be 4kg per tonne, not differing greatly from Flower & Sanjayan.

CHAPTER THREE: MATERIALS, MIX PROPORTIONS & TEST PROCEDURES

3.1 Introduction

The following chapter outlines the experimental programme and discusses the materials used and their characteristics, prior to detailing the mix proportioning and test methods used during this study.

3.2 Experimental Programme

The initial part of the research was concerned with selecting cement combinations based on BS EN 197-1, industry advice and a literature review. Control mixes of 100% Portland cement (CEM I) were cast and binary combinations of CEM I and ground granulated blast furnace slag (GGBS) were used to provide references before incorporating limestone (LS) or fly ash (FA) to give ternary blend combinations for testing. The beneficial effects of GGBS, with regard to the development of compressive strength has been studied at length over the past few decades as summarised in the previous chapter, where a number of studies examined a range of addition levels from 10 to 80%. The range of addition options is substantial and three main binary levels of 35, 55 and 75% GGBS were considered.

An additional test level of 90% GGBS was considered initially and a variety of tests carried out at this level, given that BS EN 197-1 covers cement types incorporating GGBS as a constituent ranging from 6 to 95%. However, early results were indicative of poor performance for concrete so focus was placed on the other combinations levels following industry guidance. The standard also covers the addition of limestone as a binary material up to 35%, hence levels of 10, 20 and 35% were considered in the ternary mixes.

Fly ash has been used as a binary material for many years and it use has increased threefold between 1977 and 1996 as reported by Detweiler et al (*1996*). Binary studies of fly ash cover similar addition levels to those of GGBS but as a ternary material there is very limited

reporting, the replacement values of 10 and 20% are therefore used to allow for comparison of the results with those of the limestone ternary mixes.

Figure 3.1 provides an overview of the experimental programme including both paste and concrete phases. The paste study included tests on the fresh properties of the cement combinations to provide an understanding of the effects of the cement additions in relation to the standard consistency, setting time, viscosity and developing structure prior to adding aggregate. Tests on concrete included compressive strength together with permeation and durability properties of the concrete. ISAT, air permeability and NordTest (chloride migration) were the main tests carried out with sorptivity, water penetration under pressure and rapid chloride permeability test (RCPT) providing supplementary results for confirmatory purposes.

3.3 Materials

3.3.1 Portland cement and additions

All materials used in this study were supplied from single sources in dry powder form and stored in airtight plastic containers to prevent any deterioration. The Portland cement conforming to BS EN 197-1:2000 was of strength class of 42.5N. The GGBS conformed to both BS 6699:1992 and BS EN 197-1:2000. The fly ash and the limestone met the requirements of BS EN 450-1:2005 and BS 7979:2001, respectively. These materials are typical of those used in concrete construction practice. Physical and chemical characteristics were tested and are discussed in the following section.

3.3.2 Aggregates

Coarse and fine aggregate were obtained for the concrete mixes all of which conformed to BS EN 12620:2002. The coarse aggregates used for the concrete casting was natural gravel of two size grades, 5-10mm and 10-20mm, whilst the fine aggregate was 0-4mm. The aggregates used were also low in porosity thus reducing additional water needed to be added during the mixing process by varying the quantity of fine aggregates. Whilst this would not generally be considered an issue a higher porosity could affect the absorption and permeability of concrete. The aggregates underwent characterisation tests and the results are discussed in the following section.

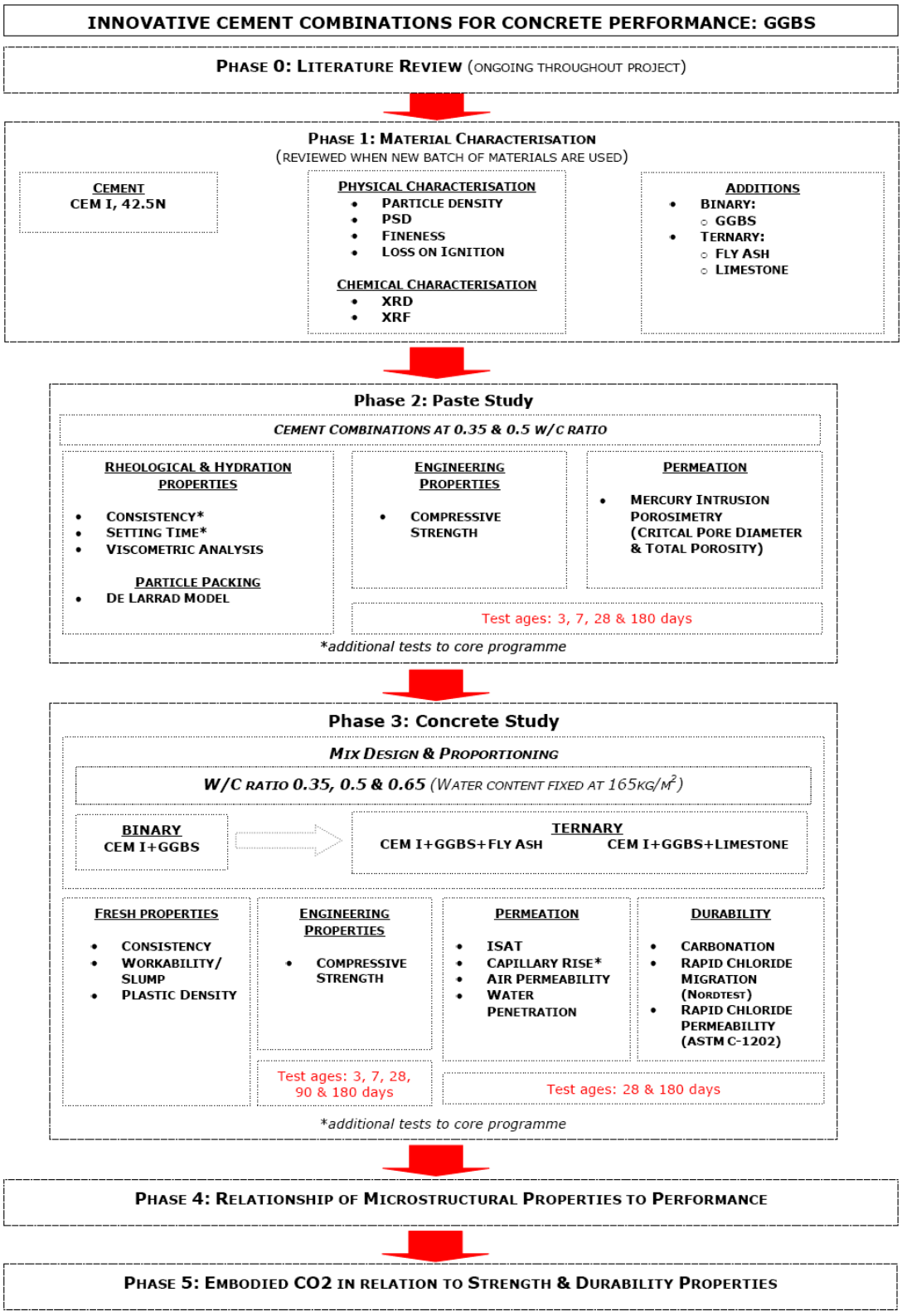


Fig 3.1: Overview of experimental programme

3.3.3 Water

Potable tap water in accordance with BS EN 1008:2002 was used to cast all paste and concrete mixes as well as being used for curing and a number of tests on the specimens. The quality of the water was important as impurities can affect the concrete. Distilled, deionised water was used to calibrate the ISAT apparatus, in addition to the test itself, and for all test procedures requiring chloride free water as part of their test procedure, including other water penetration and absorption tests.

3.3.4 Admixture

A high range water-reducing superplasticiser admixture and conforming to BS EN 934-2:2001 was used throughout the study to achieve the required consistence of 75mm nominal slump in concrete mixes at the fixed free water content.

3.4 Material Characterisation

Material characterisation was carried to ensure that all the materials used conformed to relevant standards and that there were no irregularities within their general characteristics. These tests were also carried out regularly to ensure continuity of the materials used. This procedure was specifically important when additional materials were required which, in the case of the aggregates, was with some frequency. These tests also established the properties of the individual materials to aid with the interpretation of the results from the tests on strength and durability.

3.4.1 Physical

A number of tests were carried out to establish the physical properties of the materials. The particle densities of all materials were tested in accordance with BS 812-2:1995, the results from these, summarised in Table 3.1, were required for both the Blaine test and the mix proportioning procedure. The Blaine test determined the fineness, or specific surface, of the materials and is measured in m^2/kg. The results, shown in Table 3.1, are typical of the materials used.

In addition to the Blaine test the particle size distribution of the materials was tested by "Malvern Mastersizer" equipment and software. By determining the particle size distribution of the materials the total fines content (particles passing 75µm sieve) was calculated. The fineness ultimately affects the placeability, workability and, indeed, the water content of the concrete and is necessary to establish a closed structure within the concrete, thus improving the strength and durability properties.

Loss on ignition, in accordance with BS EN 196-2, was also carried out on the CEM I, GGBS and fly ash. This test showed the extent of carbon and hydration of free lime and free magnesia.

3.4.2 Chemical Properties

In addition to the physical properties both the chemical and mineral properties of the materials were tested by X-ray fluorescence spectrometry (XRF). Powder specimens were placed into aluminium sample holders and compressed into pellets before placing into the XRF machine for testing. The results show typical bulk oxide content for the materials tested and are summarised in Table 3.1.The bulk oxide content was established to ensure that the cement conformed to BS EN 197-1, for example that the ratio of CaO to SiO_2 was not less than 2 and that the MgO content did not exceed 5% by mass. By testing the GGBS and fly ash differences in the content were seen and assisted in the interpretation of the results from the other tests on the concrete.

3.4.3 Aggregates

In addition to testing the characteristics of the cementitious materials the density and porosity of the aggregates were also tested. The results are summarised in Table 3.2. The water absorption of the aggregates showed that all were less than 3% ensuring that the effect on the porosity and permeation properties of the concrete was minimised. By understanding the properties of the aggregates better mix proportioning was possible

Table 3.1: Summary of Material characterisation results

Property	PC	GGBS	Fly Ash	LS
Fineness (m^2/kg)	409.5	450	388.5	1550*
Loss on Ignition	0.99	0.87	6.07	42.84
Particle Density	3.14	2.91	2.2	2.63
Initial Setting Time, minutes	114	-	-	-
Particle size distribution, % passing by mass				
125 µ	100	100	100	100
100 µ	99.9	97.3	98.5	100
75 µ	96.1	92.4	93.5	99.5
45 µ	86.5	84	82.2	98.1
25 µ	68.8	71.4	66.5	93.5
10 µ	37.5	44.3	40.8	71.8
5 µ	19.1	30.2	24.1	48.6
2 µ	7.7	12.8	10.9	23.6
1 µ	3.9	7.59	4.6	9.7
0.7 µ	1.8	4.1	1.9	7
0.5 µ	0.2	.9	0.1	0.2
Bulk Oxide Content				
CaO	64.63	39.59	2.8	55.31
SiO_2	20.04	35.5	43.95	0.43
Al_2O_3	4.61	12.77	21.73	0.28
Fe_2O_3	3.81	0.49	8.7	0.04
MgO	2.51	8.35	1.13	0.14
MnO	0.05	0.57	0.05	0.02
TiO_2	0.26	0.53	1.23	-
K_2O	0.64	0.54	2.31	-
Na_2O	0.34	0.18	0.82	0.05
P_2O_5	0.11	-	0.39	0.01
SO_3	3.09	-	1.26	-
C_3S	65.58	-	-	-
C_2S	8.32	-	-	-
C_3A	5.77	-	-	-
C_4AF	11.57	-	-	-

Nitrogen absorption test

Table 3.2: Summary of characteristics of aggregates used during the study

Property	Sand	Coarse Aggregates	
		5-10 mm	10-20 mm
Shape, visual	-	Rounded	Rounded
Surface Texture, visual	-	Rough	Smooth
Particle Density	2.599	2.605	
Water absorption (Lab dry to SSD), %	1.05	0.27	1.97
Grading, % passing by mass			
37 mm	-	100.0	100.0
20 mm	-	100.0	91.3
14 mm	-	100.0	48.4
10 mm	-	86.8	9.0
6.3 mm	100.0	28.3	0.8
5 mm	98.8	11.0	0.5
2.36 mm	85.3	-	-
1.18 mm	70.8	-	-
0.6 mm	54.6	-	-
0.3 mm	31.0	-	-
0.15 mm	4.0	-	-
0.075 mm	0.9	-	-

3.5 Mix Proportions & Mix Design Procedure

3.5.1 Mix Proportions

CEM I was replaced by binary and ternary materials of equal mass to give the cement combinations for the study as outlined in Table 3.3. The cement was replaced by mass so as to ascertain the benefits or limitations of reducing the CEM I content to provide concrete with an overall lower ECO_2 without compromising the strength and durability properties of concrete. A 100% CEM I control mix was produced with which the binary and ternary concretes were compared. The GGBS levels were chosen to give a wide range to the study and represent those

more widely used and tested in previous studies and covered by standards, enabling a comparison of ternary additions. With regards to the limestone, the addition ranged from 10 to 35%, the maximum allowable under BS EN 197-1.

A fixed water content of 165 l/m^3 was used for concrete mix designs with water/cement (w/c) ratios of 0.35, 0.5 and 0.65. Superplasticiser dosage (Glenium 51) was adjusted for each mix in order to give a nominal slump of 75 ± 25mm in accordance to consistency class S2 in BS8500. The range of w/c ratios allowed for a broad range of strengths in BS 8500.

Table 3.3: Cement combinations used during the study

Mix No	PC	GGBS	FA	LS
1	100	-	-	-
2	65	35	-	-
3	65	25	10	-
4	65	25	-	10
5	45	55	-	-
6	45	45	10	-
7	45	35	20	-
8	45	45	-	10
9	45	35	-	20
10	25	75	-	-
11	25	65	10	-
12	25	55	20	-
13	25	65	-	10
14	25	55	-	20
15	25	40	-	35
16	10	90	-	-
17	10	70	-	20
18	10	55	-	35

Mix proportions were established for all combinations at all water cement ratios; 0.35, 0.5 and 0.65 to give low, medium and high strength concretes, and provided an insight into the effects of w/c ratio on the combinations. Barnett et al (*2006*) tested concretes over three water/binder ratios (0.25, 0.4 and 0.6) corresponding to 28 day target mean strength of 40, 70 and 100 N/mm^2. Babu & Kumar (*2000*) tested a w/b ratio range of 0.23 to 0.83.

3.5.2 Mix Design

The BRE (British Research Establishment) mix design method was used for the purposes of this study and is a well-established concrete production procedure in the UK. Strength, workability and durability of concrete are taken into consideration when the following procedure is followed:

i. Selection of w/c ratio and water content.
ii. Calculation of cement content (water content divided by the w/c ratio).
iii. Calculation of the total aggregate content by estimation of concrete density from graphs provided in the BRE mix design procedures. This value is subtracted from the cement and water content giving the total aggregate content.
iv. The proportion of sand is then determined as a percentage of the total aggregate content. This percentage is determined by establishing the percentage of sand which passes a 600_m sieve.
v. The course aggregates content is calculated by subtracting the sand content from the total aggregates content. This is then divided into a ratio of 1:2 to give 4/10mm and 10/20mm coarse aggregate content. This is consistent with the view held by Neville (1995) who stated that a fine content of between 34% - 36% is generally applicable for concrete.
vi. Adjustment of the final water content is made to account for aggregate water absorption. This is necessary as all the normal-weight aggregates are added to the mix in a “lab dry” state rather than a saturated surface dry state (SSD) on which the BRE mix proportioning design procedures is based.

As previously stated the chosen w/c ratios of 0.35, 0.5 and 0.65 for this study provide a viable range of testing for the materials selected the mid to higher w/c ratio also reflect the recommended w/c ratios for particular exposure conditions in BS 8500. The mix proportions for each w/c ratio are shown in Table 3.4. In order to maintain yield minor adjustments were made and were necessary to ensure the expected yield of concrete was obtained. These adjustments were based on the measured particle density of the constituent materials and the mix proportions are shown in Tables 3.4(a) to (c). *Appendix A-1* provides examples of the mix design technique carried out for this study.

Table 3.4(a): Mix Proportions at 0.35 W/C ratios fixed at 165kg/m³ *

Mix No	Cement Additions				Sand	Aggragates		SP, %
	CEM I	GGBS	FA	LS		5/10mm	10/20mm	
1a	478	-	-	-	606	392	785	0.35
2a	309	167	-	-	604	391	782	0.20
3a	309	122	45	-	604	391	782	0.20
4a	309	122	-	47	604	391	782	0.20
5a	214	261	-	-	603	390	780	0.20
6a	214	213	45	-	635	389	780	0.20
7a	214	165	90	-	635	389	780	0.20
8a	213	213	-	47	601	388	779	0.20
9a	214	165	-	90	635	388	779	0.25
10a	119	355	-	-	630	389	779	0.30
11a	120	305	50	-	630	388	778	0.30
12a	120	255	95	-	630	388	778	0.30
13a	120	305	-	50	630	387	778	0.30
14a	120	255	-	95	630	387	778	0.35
15a	120	190	-	165	625	388	778	0.35
16a	50	420	-	-	625	388	778	0.35
17a	50	320	-	100	625	386	776	0.30
18a	50	270	-	150	620	386	776	0.35

**Yield corrected*

*Table 3.4(b): Mix Proportions at 0.5 W/C ratios fixed at 165kg/m³ **

Mix No	Cement Additions				Sand	Aggregates		SP, %
	CEM I	GGBS	FA	LS		5/10mm	10/20mm	
1b	333	-	-	-	655	417	833	0.12
2b	216	116	-	-	651	414	823	0.10
3b	215	80	33	-	651	414	823	0.10
4b	215	80	-	33	651	414	823	0.12
5b	150	182	-	-	650	413	826	0.15
6b	150	150	33	-	650	413	826	0.15
7b	150	115	65	-	650	413	826	0.15
8b	150	150	-	33	650	413	826	0.20
9b	150	115	-	60	650	412	825	0.25
10b	83	250	-	-	649	413	825	0.20
11b	83	215	33	-	649	413	825	0.20
12b	83	182	70	-	649	413	825	0.20
13b	83	215	-	33	649	411	822	0.20
14b	83	182	-	70	649	411	822	0.25
15b	83	130	-	120	646	411	822	0.25
16b	30	300	-	-	648	412	824	0.20
17b	30	230	-	70	646	411	824	0.25
18b	30	180	-	120	646	411	823	0.25

**Yield corrected*

*Table 3.4(c): Mix Proportions at 0.65 W/C ratio fixed at 165kg/m³**

Mix No	Cement Additions				Sand	Aggregates		SP, %
	CEM I	GGBS	FA	LS		5/10mm	10/20mm	
1c	256	-	-	-	685	430	859	0.05
2c	165	90	-	-	683	429	857	0.15
3c	165	65	25	-	683	429	857	0.15
4c	165	65	-	25	683	429	857	0.15
5c	115	140	-	-	683	428	857	0.15
6c	115	115	25	-	683	428	857	0.10
7c	115	90	50	-	683	428	857	0.10
8c	115	115	-	25	682	428	854	0.10
9c	115	90	-	50	682	428	854	0.15
10	65	190	-	-	682	427	856	0.15
11c	65	165	25	-	682	427	856	0.10
12c	65	140	50	-	682	427	856	0.10
13c	65	165	-	25	680	426	856	0.10
14c	65	140	-	50	680	426	854	0.15
15c	65	100	-	90	680	426	854	0.20
16c	25	230		-	679	426	852	0.20
17c	25	180	-	50	678	426	852	0.20
18c	25	140	-	90	678	426	852	0.25

**Yield corrected*

3.5.1 Batching and Specimen Casting

A number of test specimens were required to be cast for the experimental programme. The total number of each specimen cast was required in order to calculate the total volume of concrete to be cast. Table 3.5 outlines the specimens required for each test and the volume of each. 10% wastage is added to the total volume and given that the capacity of the pan mixer used is 0.035 two batches were required to be mixed for each combination.

Table 3.5: Specimens for casting

Specimen Size	*Test*	*Specimen number required*	
100mm^3	Compressive Strength	2 each@3,7,28,90 & 180 day	= 10
	Air permeability	2 each@ 28 & 180 day	= 4
	Carbonation	2 each @ 2, 4, 8,12 & 20 wks	= 10
	Capillary Rise	2 each @ 28 & 180 day	= 4
		Total	28
150mm^3	Water Penetration Under Pressure	2 each @ 28 & 180 days	= 4
	ISAT	2 each @ 28 & 180 days	= 4
		Total	8
100mm x 300mm cylinder	Chloride Ingress	2 each @ 28 & 180 days	= 4
		Total	4

3.6 Preparations & Preconditioning

3.6.1 Mixing

Cement Paste

The mixing of the cement combination pastes was carried out in accordance with BS 196-3 in order to achieve uniformity in the samples for testing. A quantity of water was weighed and placed into the mixing bowl of a Hobart mixer. Materials were weighed to a total of 500g and added to the water carefully to avoid any loss of material or water. The mixer was run at a low speed for 90 seconds and then stopped for 15 seconds during which time any paste adhering to the side of the bowl out with the mixing zone can be returned to the mix using the palette knife. The mixer was then run for a further 90 seconds. The total mixer running time from “zero” to completion was no more than 3 minutes. The capacity of the mixer was 5 litres which required that multiple batches were produced for all the test specimens.

Concrete

Following BS EN 12390-2:2000 the concrete samples were produced using a horizontal forced-action pan mixer with a maximum capacity of 0.035m^3. Each quantity of concrete produced was more than 10% required for the sample casting to allow for any wastage and prior to mixing aggregate was left for up to 24 hours to ensure it was used in a laboratory dry condition.

Air drying the aggregate allowed for the removal of surface water, or aggregate-free water that can become part of the total batch water as soon as the mixing process began. The mixing procedure takes into account the surface dry aggregate and some of the batch water is absorbed into the aggregates during the initial stages of the process which involved adding half the required water to the aggregates, after dry mixing for 1 minute, and leaving covered for 8 minutes to allow for water to be absorbed. The cement and additions were then added and mixed for a further minute prior to adding the superplasticiser and remaining water and mixing for a further 2 minutes. To ensure complete homogeneity the mixed concrete was then hand mixed using a trowel.

It was standard practice to carry out both workability and plastic density tests on each of the mixes within 15 minutes of mixing in accordance with BS EN 12390-2:2000. Slump was tested to ensure the nominal slump of 75 ± 25mm was achieved and the concrete's workability evident. Due to its surface texture GGBS can create higher workability which is not always evident with the slump test (*Tattersall, 1991*). The plastic density of concrete was determined in accordance with the method described in BS EN 12350-6 (BSI, 2009). A cylindrical container was placed on a vibrating table filled in five equal layers, with each layer vibrated for 15 seconds. The plastic density of the concrete in kg/m3 was determined by dividing the weight of the compacted concrete by the volume of the container. Both tests were carried out within 15 minutes of mixing and prior to casting within a further 15 minutes.

3.6.2 Casting & Curing

The mixed concrete was then placed into prepared moulds and left to cure for an initial 24 hours, covered in damp hessian and plastic sheeting, prior to de-moulding. The de-moulded specimens were placed in water curing tanks with a controlled temperature of 20°C ±1° until required for testing. Table 3.5, previously, shows the curing days required for each of the selected tests, together with the specimen sizes cast.

3.7 Fresh Properties of Paste

3.7.1 Standard Consistency

Standard consistency tests were carried on the paste samples to determine the water requirements for each combination of materials. In accordance with BS EN 196-3, each combination sample was prepared. The Vicat was set up with the plunger shown in Figure 3.2, attached and calibrated by lowering to rest on the base plate and adjusting the pointer to read zero.

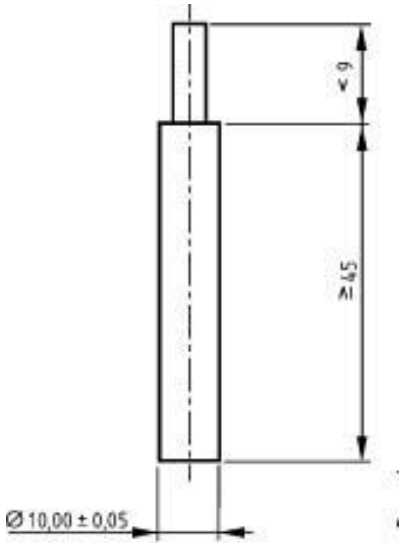


Fig 3.2: Vicat plunger for standard consistency test

The methodology laid out in the standard was followed to determine the standard consistency and it was often necessary to repeat this test with different water contents until the results showed a distance of 6mm (±1mm) between the plunger and base-plate. The water quantity was recorded, together with the mass and volume of each of the tested samples. This

test indicated the influence of the different additions on the water demand of the cement paste and results are expressed in terms of water/cement ratio.

3.7.2 Particle Packing

The De Larrard (1999) Compressible Packing Model (CMP) was used to determine the particle packing for the constituent materials. According to this model, the packing density ν is given in the following implicit equation:

$$K = \sum_{i=1}^{n} K_i = \sum_{i=1}^{n} \frac{y_i / \beta_i}{\frac{1}{\varphi} - \frac{1}{\gamma_i}})$$

[Eq 3.1]

with:

$$\gamma_i = \frac{\beta_i}{1 - \sum_{j=1}^{i-1} \left[1 - \beta_i + b_{ij} \beta_i \left(1 - 1/\beta_j\right)\right] y_j - \sum_{j=i+1}^{n} \left[1 - a_{ij} \beta_i / \beta_j\right] y_j}$$

[Eq 3.2]

where, K is called Compaction index.

K_i is the contribution of class *i* to the compaction index.

β_i is called virtual packing density of a monodisperse mix (comparing to a_i in LPM).

γ_i is virtual packing density of a polydisperse mix, when the *i* fraction is dominant (comparing to φ_i in LPM).

a_{ij} is the loosening effect coefficient, and

b_{ij} is the wall effect coefficient (comparing to f(*i,j*) and g(*i,j*) in LPM).

This model gives a better prediction of the packing density than the linear packing model (LPM) and has smoothed curves near the maximum packing point. In the concept of the CPM, the new introduced parameter *K* depends only on the packing process. Virtual packing density, which was determined by the LPM, is the maximum packing density achievable with the given mixture and refers to the situation of *K* = 4. Figure 3.1 shows the calculated packing density

changing with the *K* values with a size ratio of 1/8 after the compressible packing model. Actual packing densities of the two classes are assumed to be equal to 0.64, and the different curves stand for low to high K values. (De Larrard, 1999, re-drawn)

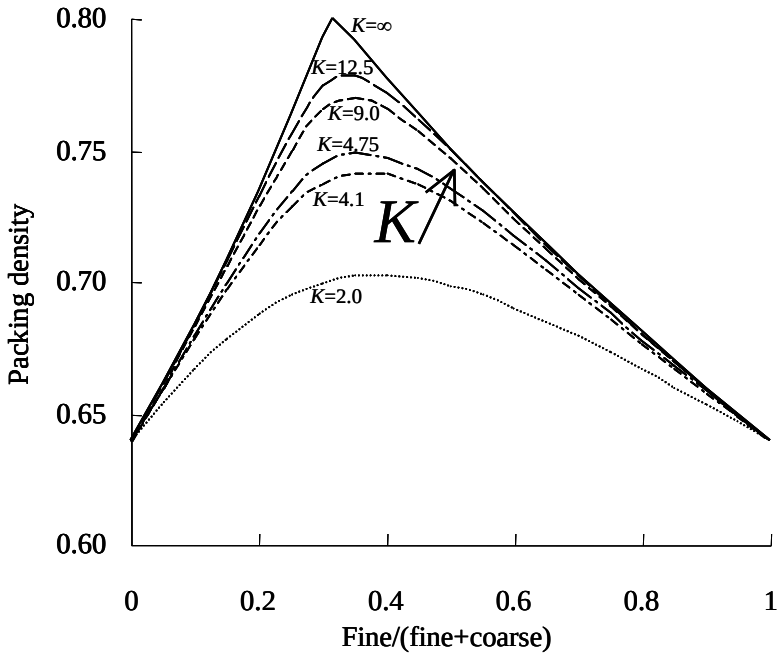


Fig 3.1: Packing density of binary mix of grain.

Based on test data, De Larrard got the *K* values for different packing processes as shown in the Table 3.2. The new functions to determine the loosening and wall effects are:

$$a_{ij} = \sqrt{1-(1-d_j/d_i)^{1.02}}$$
$$b_{ij} = 1-(1-d_i/d_j)^{1.50}$$

[Eq 3.3]

Table 3.6: K values for different packing processes in De Larrard's CPM.

Dry packing				Wet packing
Pouring	Sticking with a rod	Vibration	Vibration + compression 10 kPa	Smooth, thick paste
4.1	4.5	4.75	9.0	6.7

3.7.3 Setting Time

In accordance with BS EN 196-3 this procedure was undertaken using automatic calibrated setting time equipment. Setting time tests were carried out on both 0.35 and 0.5 water/cement ratio pastes and the data logged to show the initial and final setting times for each combination tested. Tests were carried out on these w/c ratios as they would then allow comparison with the properties tested on concrete. This test would also, ultimately allow for planning in the placement of concrete on site. Both GGBS and fly ash can extend the initial setting time as discussed in the previous chapter.

3.7.4 Viscometery

A Brookfield viscometer was used to establish the yield stress and viscosity of the cement combination pastes. The cement paste was mixed and 70 ml then placed into a 100ml plastic beaker. The viscometer was placed such that the spindle was in the centre of the beaker and as it moved up and down stoppers were located to prevent the spindle from leaving the paste and touching the bottom of the beaker.

As the spindle rotated readings were taken every 30 seconds and 3 times for each speed to give an average. The results were then plotted and a best fit line drawn through all corresponding shear stress (torque) and rate of shear values (rotational speed) as shown. The equation of this line gave the values for plastic viscosity (slope angle) and yield stress (x-axis intercept). The viscosity of the cement paste will have some influence on the downward movement, or segregation, of the aggregates within the concrete, with major values mitigating this.

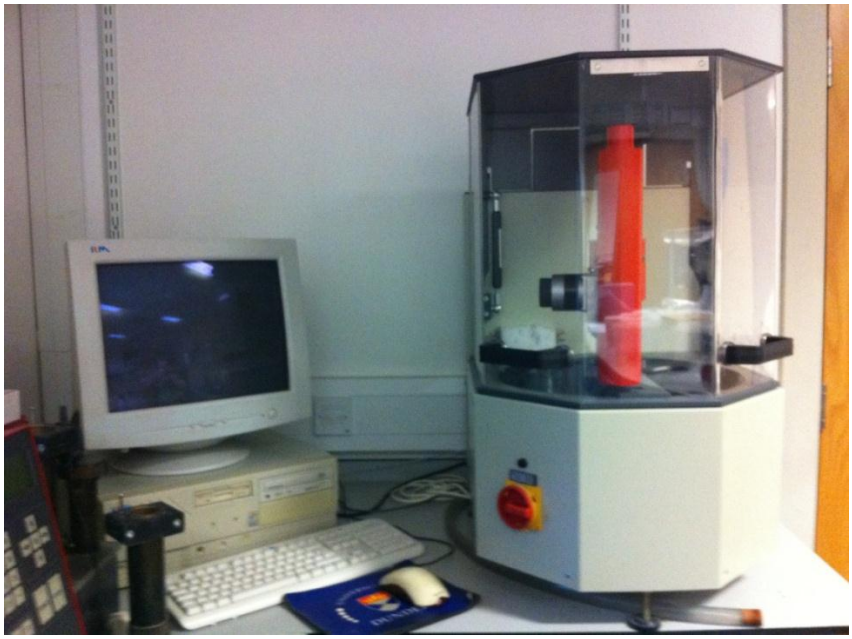


Fig 3.3: Automated Setting Time Equipment

Fig 3.4: Brookfield Viscometer

3.8 Mercury Intrusion Porosimetry

An automated mercury intrusion porosimeter (Figure 3.5) was used to measure the pore size and the porosity of paste samples. Low pressure testing is carried out prior to high pressure testing and the data produced is combined to give the final result.

Fig 3.5: Mercury Intrusion Porosimeter Equipment

Each specimen is no more than 10mm in diameter and placed into the glass cell which is loaded into the porosimeter which is capable of measuring 950 micron to 0.0064 micron pore diameter. The test was only carried out on paste specimens. Indeed, the aggregates in the concrete specimens would affect the results of the porosity test due to their size with respect to the sample; it may be possible that a specimen may only consist of aggregate and no cement paste.

The relationship between the applied pressure and the pore diameter into which the mercury will intrude is given by the Washburn equation (*Hanzick, 2010*):

$$D = \frac{-4y\cos\theta}{p}$$

[Eq 3.4]

Where p is the applied pressure
D is the pore diameter
Y is the surface tension of the mercury (480 dyne cm^{-1})
ϑ is the contact angle between the mercury and the pore wall, usually taken as 140^{o}.

3.9 Compressive Strength

Compressive strength tests were carried out in accordance with BS EN 12390-3:2002 (Testing hardened concrete – Part 3: Compressive strength of test specimens) and reported to the nearest $0.5N/mm^2$. By testing specimens at a variety of ages (3, 7, 28, 90 and 180 days) the effects of w/c ratios and cement additions on the rate of development of compressive strength was determined.

3.10 Permeation & Absorption Properties

It is important for concrete to be able to withstand many conditions that may affect the rate of deterioration adversely. The permeation and absorption of liquids, ions and gases into the concrete can be detrimental to the steel rebar reinforcement, causing corrosion, within the concrete structure. It is therefore fundamental to understand the effect additions have on reducing the rate of permeation and absorption of liquids, ions and gases and this can be achieved, to some extent, by carrying out the following tests that cover a range of permeability and absorption properties.

3.10.1 Initial Surface Absorption Test (ISAT)

This is one of the most commonly used tests for assessing the durability of concrete (*Kumar & Bhattacharjee, 2002*). It has been used by a number of previous studies including Bungey, 1989; Garboczi, 1990; Mehta & Monterio, 1993; Basheer et al, 2005. The procedure laid out in BS 1881: Part 208: 1996 (“Recommendations for the determination of the initial surface absorption of concrete”) was followed. Tests were carried out at both 28 and 180 days on two 150mm cubes that were oven dried to a constant mass and the apparatus was set up as shown in Figure 3.6.

The ISAT apparatus was calibrated and the rubber seal was lightly greased and clamped centrally onto the side surface of the specimen to ensure a watertight seal. Water from the reservoir, with a 200 ± 20mm head, flowed through the tubing when the tap was opened and when it first reached the concrete surface a stopwatch was started and then flow stopped 15 seconds prior to 10 minutes having elapsed. The distance the water surface moved along the capillary tube was recorded and an ISA-t value was obtained by using the following formula:

$$ISAT - t\,value\left(ml/m^2/s\right) = d\,x\,F \qquad [Eq\ 3.5]$$

Where, *d* is the distance moved by water (mm) at time, t (mins)

F is the calibration factor for apparatus

The mean ISAT-10, 30 and 60 values were reported to the nearest 0.1×10^{-2}. The initial surface absorption is defined as the rate of water flow into concrete per unit area at the stated interval (10 minutes) from the start of the test at a constant applied head of 200mm at room temperature.

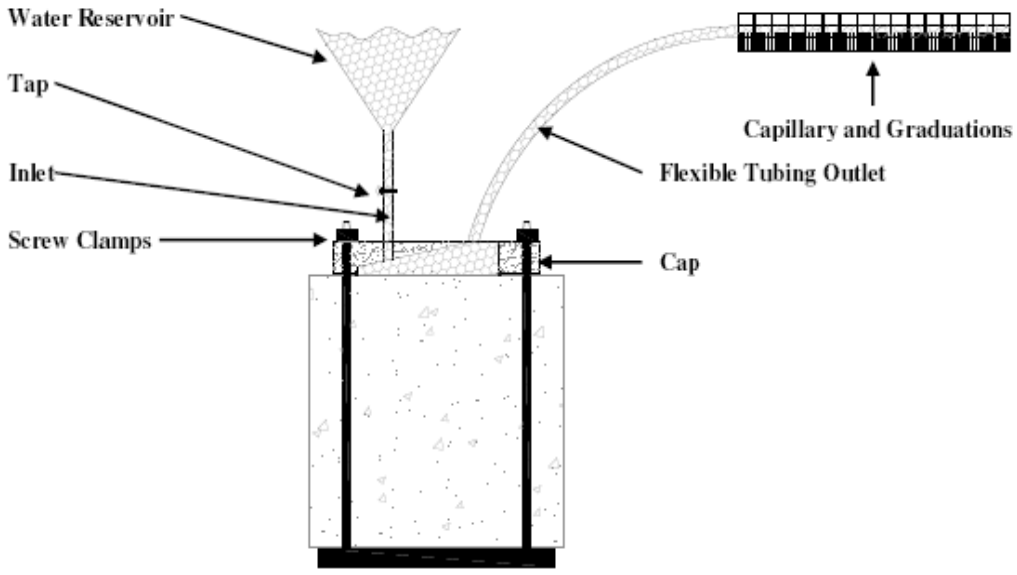


Fig 3.6: Schematic diagram showing the ISAT equipment set-up.

3.10.2 Sorptivity

The sorptivity of the test specimens at ages 28 and 180 days is tested by following the method outlined in ASTM C1585-04. This test was used selectively for conformity purposes given its coverage in a number of previous studies and determines the susceptibility of an unsaturated test sample to the penetration of water by absorption, measuring the sorptivity of the concrete by means of capillary suction. This test differs from the ISAT in that the total water flow measured is the sum of capillary and gravity driven flows. Two specimens of 100mm diameter and 50mm thickness were cut from a 300mm cylinder and then oven dried to constant mass and cooled to room temperature and the weight recorded. The sides of each specimen was sealed with wax and then placed onto small supports so that only the lower 2 to 5mm was submerged. The top of the specimens were covered to prevent moisture loss by evaporation. A schematic of the test set-up is shown in Figure 3.7. At timed intervals (1, 5, 10, 20, 40 and 60 minutes) and, thereafter, every 60 minutes up to 6 hours from the start of the test, the specimens were weighed (to the nearest 0.1g) and the water level on the specimen also recorded. The accumulated water absorption is then calculated using the following equation:

$$i = \Delta m / A\rho$$

[Eq 3.6]

Where, i is water absorption

Δm is the increase in weight by water absorption of the specimen

A is the test surface area

ρ is the density of water

From Darcy's Law it can then be derived that the cumulative water absorption increases with the square root of time:

$$i = S\, t^{1/2}$$

[Eq 3.7]

Where, i is water absorption

S is the sorptivity of concrete (mm/sec $^{1/2}$)

$t^{1/2}$ is the time (sec $^{1/2}$)

The sorptivity is determined as the slope of i against $t^{1/2}$, which can be obtained by a least square fit of i on $t^{1/2}$. This can be ascertained by plotting the data to give a coefficient form the trend-line equation as shown in the sample chart in Figure 3.8. *Appendix A-2* provides an example of the spread-sheet used to determine the coefficient; this was completed with the weight at each timed interval for each of the samples tested.

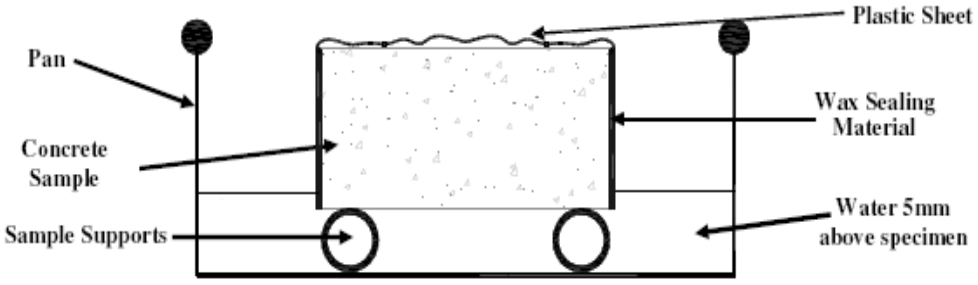


Fig 3.7: Schematic of the sorptivity test

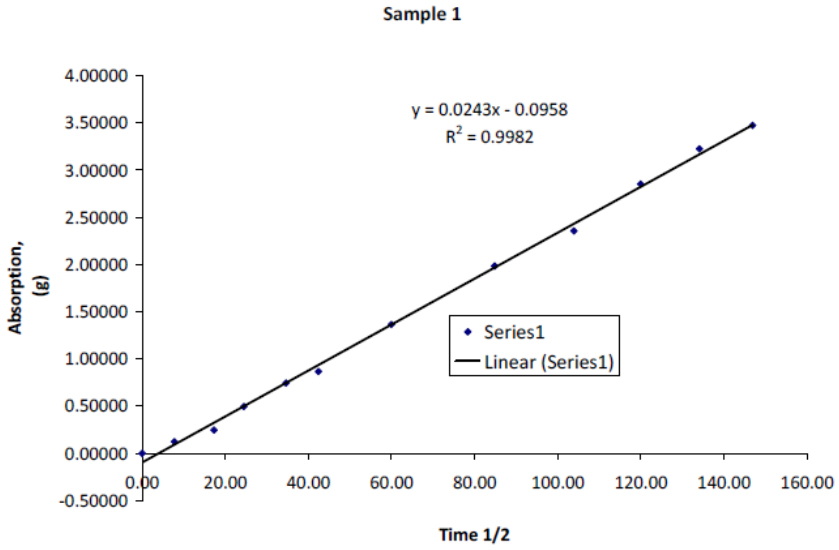


Fig 3.8: Sample chart indicating the sorptivity coefficient (y=0.0242)

3.10.3 Air Permeability

No standard exists for this particular test. The method used followed that of the "University of Dundee Method" as described by Dhir et al (*1989*). Cubes of 100mm diameter were cast and then a 54mm diameter core taken and sliced to give two specimens of approximately 50mm length. These cores were then oven dried and cooled to room temperature before testing.

The length of each prepared core was measured at three points around the circumference to obtain an average length prior to lightly greasing the outside surface of the specimen and placing it into the air permeability apparatus. Figure 3.9 shows a schematic of the air permeability apparatus.

An oil pressure of 300psi was applied to the circumference of the specimen then a uniaxial air pressure up to a maximum inlet pressure of 2.76 N/mm^2 was applied. Readings are taken from the outflow meters at pressures 110, 90, 70, 50 and 30 psi. *Appendix A-3* shows an example of the spread-sheet used to calculate the intrinsic permeability (k) which was determined by using the following formula and reported to the nearest 0.1 m$^2\times10^{-17}$.

$$k = \frac{2\mu L P_2 Q_2}{A\left(P_1^2 - P_1^2\right)}$$

[3.8]

Where
- Q_2 is the outlet volume rate of flow, cc/min
- P_1 is the inlet pressure, psi
- P_2 is the outlet pressure (atmospheric)
- A is the cross-sectional area of specimen, mm^2
- L is the average length of specimen, mm
- μ is the dynamic viscosity of air

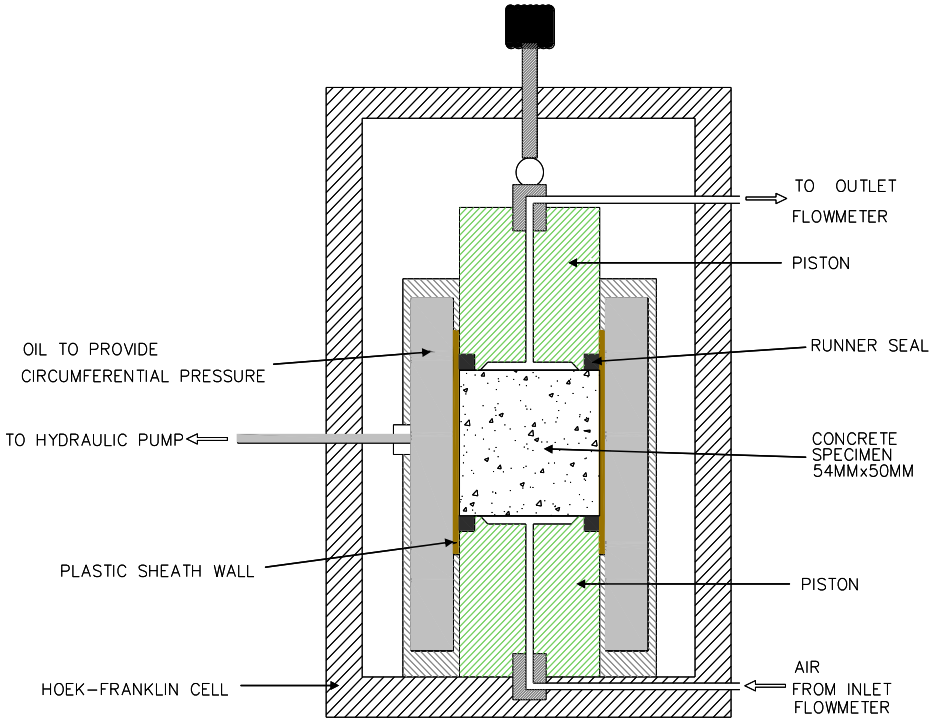


Fig 3.9: Layout the air permeability apparatus (Dhir et al, 1989)

Fig 3.10: Air permeability testing equipment

3.10.4 Water Penetration Under Pressure

Water penetration is carried out in accordance with BS EN 12390-8. A 150mm cube specimen was clamped into the testing rig and a pressure of 0.7 MPa for 72 hours applied to the roughened surface. In this case no preconditioning of the specimen was required; the specimen was removed from the curing tank at the required test age. A schematic diagram of the test set-up is shown in Figure 3.11. The specimen was removed after the indicated test time and split perpendicular to the roughened surface to enable measurement of the water penetration indicated by darker, damp areas on the rough surface of the concrete sample. This depth of penetration was recorded in depth by millimetres.

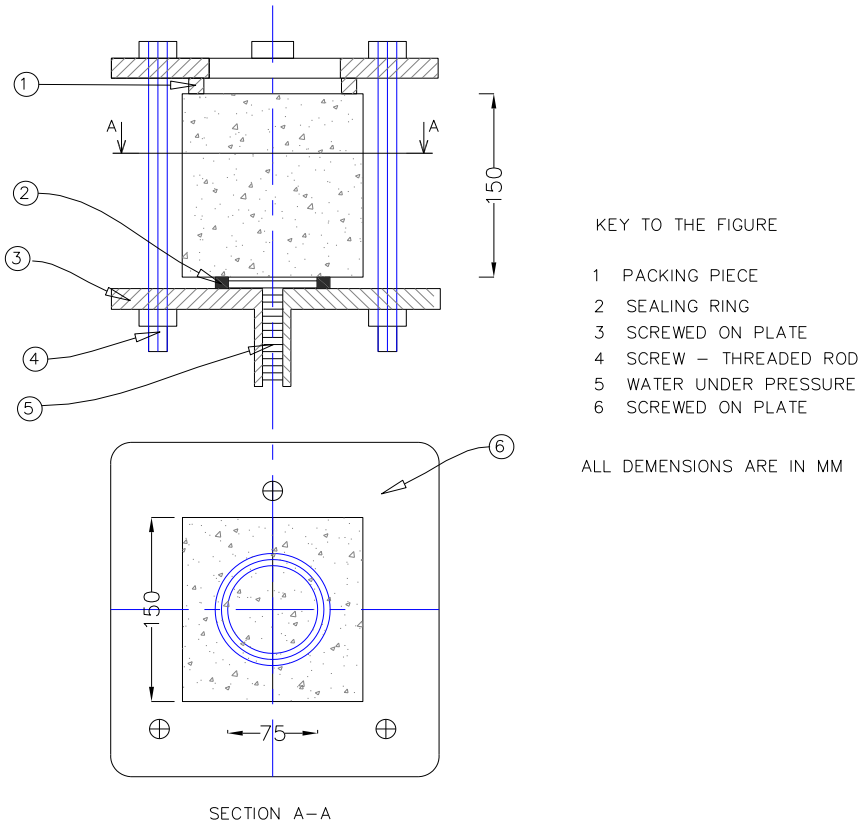


Fig 3.11: Layout the water penetration under pressure apparatus

3.11 Durability

As with previous tests, whilst GGBS binary concretes have been tested extensively with regard to their durability properties, less is known, to date, on the effects ternary additions have with regards to the ingress of carbon dioxide or chloride. To this end, the following tests were carried out on the cement combinations in concrete.

3.11.1 Carbonation

The poor resistance of GGBS concretes to carbon dioxide has been widely reported in the past. However, there is limited understanding as to the effects of ternary additions such as fly ash and limestone and whether they are detrimental or of benefit to concrete in reducing carbonation. Carbonation itself is a lengthy process and takes many years to occur. Furthermore, it does not cause deterioration to concrete directly but affects the durability of reinforced concrete as its penetration to the steel will cause corrosion. Accelerated carbonation tests were carried out using the method developed by Dhir et al (*1985*) on selected combination concrete mixes. 100mm cube specimens were air dried at 20^{o}C, and 55% relative humidity for 14 days after 28 days water curing. They were then coated with silane primer and paraffin wax on 5 faces leaving an open cast side face, before placing in a carbonation tank with an enriched 4.0% CO_2 environment at 20^{o}C and relative humidity of 50% ±5% for 2, 4, 8, 12 and 20 weeks. At the test age they were removed, split and the freshly broken surface treated with a solution of 2.0% phenolphthalein, 48.0% distilled water and 50.0% ethyl alcohol. Measurement of the colourless (carbonation zone) were taken at 5 points to give an average depth of carbonation.

3.11.2 Non-steady State Rapid Chloride Migration

The NordTest method (*NT Build 492*) determines the chloride migration coefficient from non-steady state migration. Each specimen consists of a 50mm slice taken from the central portion of a cast Ø 100mm x 300mm cylinder. After being surface dried, the specimen was placed in a vacuum for 3 hours at a pressure of 10-50 mbar, prior to being saturated with limewater for a further hour. The specimens were then placed into the apparatus as shown in the schematic diagram in Figure 3.12 below.

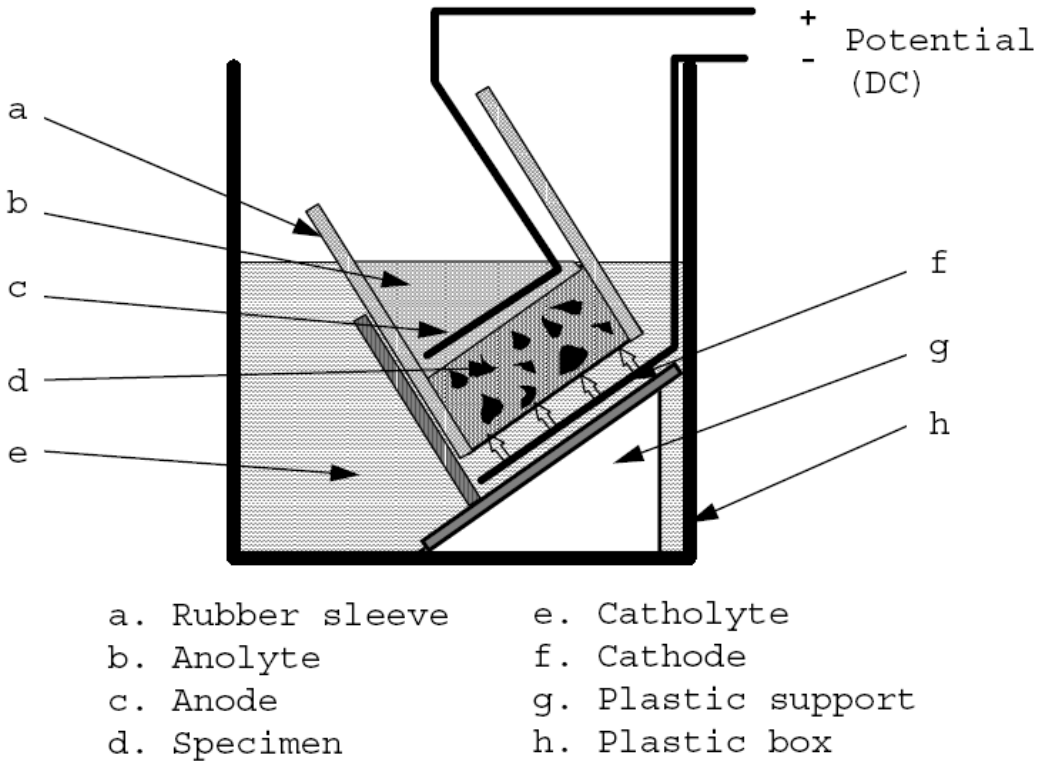


Fig 3.12: Schematic diagram of the set-up of the apparatus for NordTest Method. (NT Build 492, 1999)

The rubber sleeve was fitted and secured by 2 clamps; silicon sealant was used to improve their tightness, prior to placing the specimen on the support in the catholyte reservoir. The sleeve above the specimen was filled with 300ml anolyte solution (0.3 M NaOH) and the anode then immersed. An external electrical potential of 60V was applied axially across the specimen, forcing the chloride ions to migrate from outside to inside the specimen.

The chloride penetration depth was then measured by splitting the specimens axially and spraying a concentration of silver nitrate solution onto the split surfaces as shown in Figure 3.13. The chloride coefficient was the calculated using the following equation, a modification of Fick's second law (*Tang & Nilsson, 1992*):

$$D_{appm} = \frac{0.0239(273+T)L}{(U-2)t}\left[x_d - 0.0238\sqrt{\frac{(273+T)Lx_d}{U-2}}\right]$$

[3.9]

Where, D_{appm} is the apparent non-steady state migration coefficient, $m^2/s \times 10^{-12}$

U is the applied potential, V

L is the specimen thickness, mm

T is the average value of the initial and final temperatures in the anolyte solution, ^oC

x_d is the penetration depth, m

t is the test duration, sec.

3.11.3 Rapid Chloride Permeability

In addition to the NordTest Method, the ATSM C-1202 method for determining the rapid chloride permeability of a test specimen was also used. With regard to the literature, this appeared to be the most commonly used method in other studies and whilst the NordTest is becoming more widely accepted as a method for testing rapid chloride migration it was considered beneficial to investigate the concretes using the RCPT. This test has been used by both Hooton & Titherington (*2004*) and Becknell & Hale (*2005*) to evaluate the electrical conductance of the concrete specimens to provide an indication of their resistance to chloride ion penetration. The test method requires that each specimen is conditioned by covering it with distilled de-aerated water and placed in a vacuum desiccator with the vacuum maintained for 4 hours. The specimen is then soaked for a further 18 hours prior to placing them into the test cells as shown in the schematic diagram in Figure 3.14.

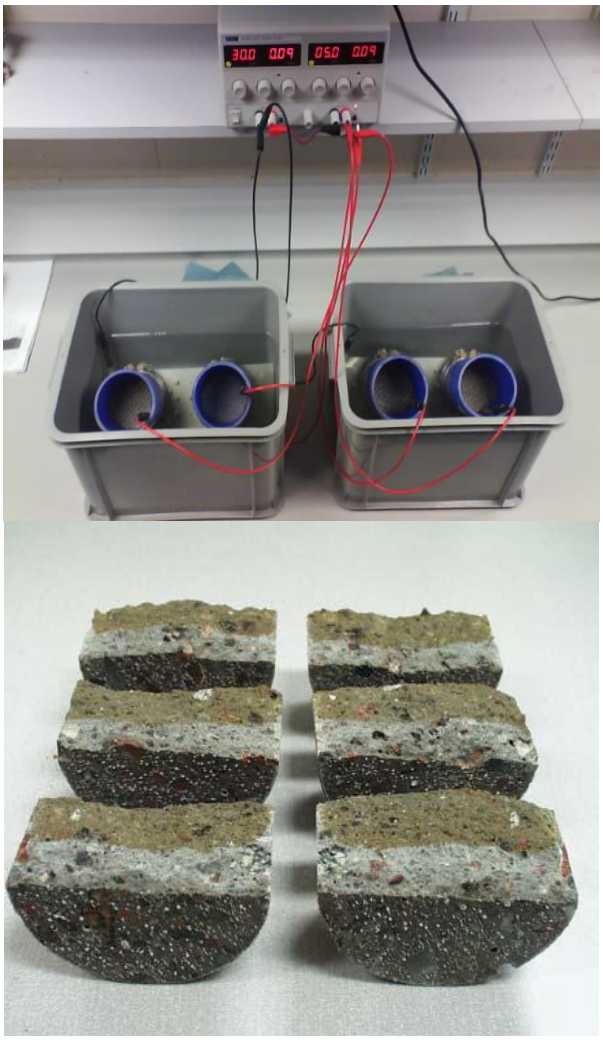


Fig 3.13: NT Build Test specimens

Water was poured into the cell to ensure that it was watertight and then removed and the cell filled with the test liquids (3.0% NaC1 and 0.3 N NaOH solutions) in the two cell reservoirs. The level of the liquids has to be 2-3 mm below the filling tubes of the cell parts. The prepared specimen cells are then linked to the PROOVE'it™ Microprocessor Power Supply unit as shown in Figure 3.15, and the test run. Each cell is connected only to each channels power supply binding posts (red jack to red binding post and black jack to black binding post). As with the NordTest the data was used to calculate a chloride migration coefficient from the modification of Fick's second law.

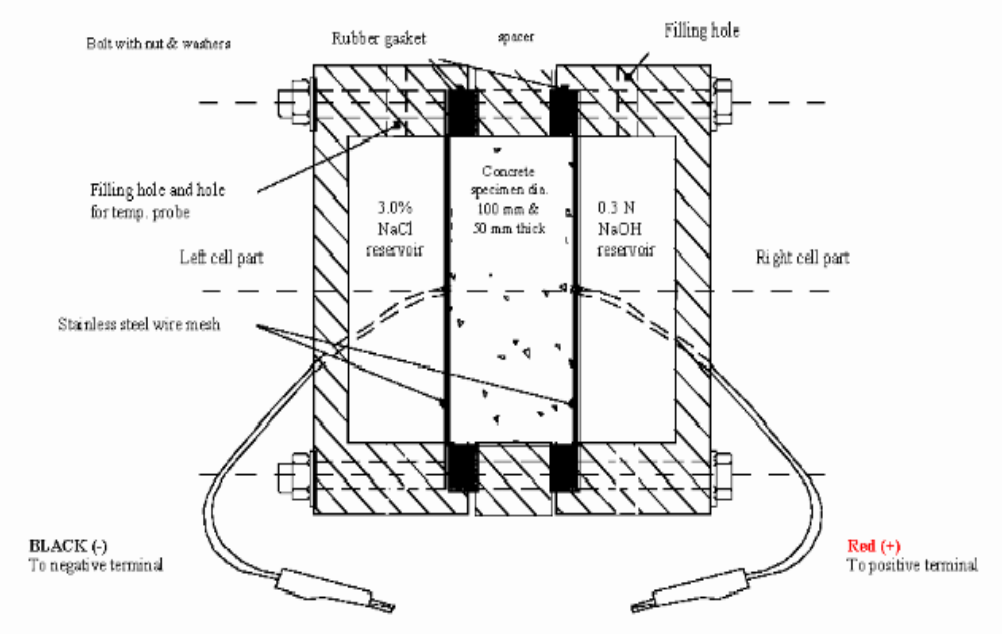


Fig 3.14: The assembly of the test cell for rapid chloride penetration tests.

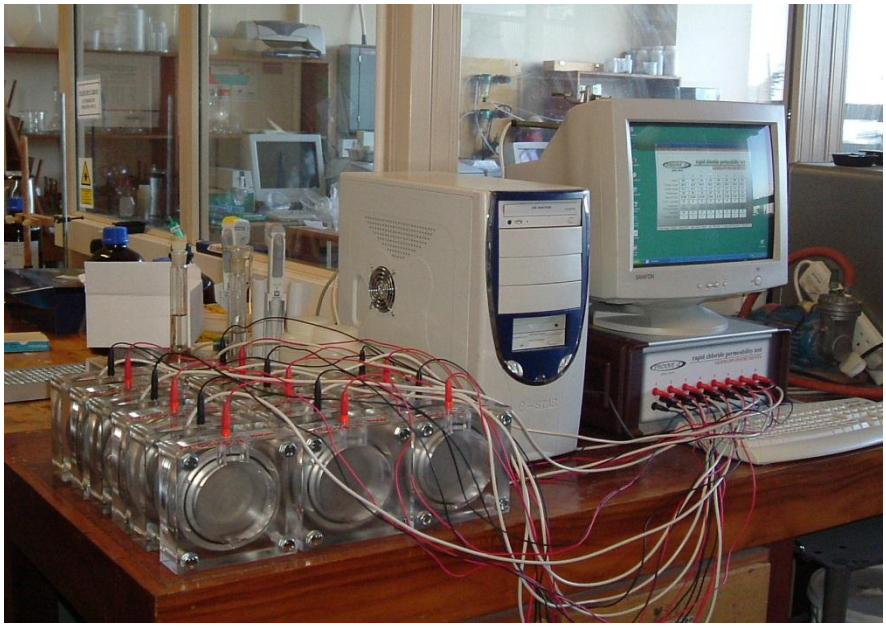


Fig 3.15: The prepared specimens connected to the PROOVE'it™ Microprocessor

3.12 Calculating Embodied CO_2 (ECO_2)

It was previously shown in Chapter 1 that the use of blended cement combinations in the construction industry is limited to a number of specific case studies. In order for application levels to change, standards and legislation need to evolve to permit greater use of GGBS, fly ash and other additions, but this cannot occur without further research into the effects additions have on the strength and durability of concrete. As part of this, evaluation of the environmental impact of concrete should also be made. Based on information already covered in Chapter 2 the ECO_2 of each blended combination concrete was calculated for each tonne of concrete produced follow the formula shown in equation 3.5 which takes into consideration the estimated ECO_2 for each component of the concrete.

$$ECO_2 = (CEMI \times 0.93) + (GGBS \times 0.052) + (FA \times 0.004) + (LS \times 0.032) + (W \times 0.003) + (A \times 0.004) \quad [3.10]$$

Where,
- *CEM I* = *Portland cement*
- *GGBS* = *Ground glass blast-furnace slag*
- *FA* = *Fly ash*
- *LS* = *Limestone*
- *W* = *Water*
- *A* = *Aggregates*

The ECO_2 of all concrete combinations is summarised in Figure 3.16, *Appendix A-4* provides the tabulated data. These calculations were then used to assess the ECO_2 of the concrete mixes in relation to the strength, permeation and durability properties in order to consider the environmental impact of binary and ternary concrete compare to CEM I concrete.

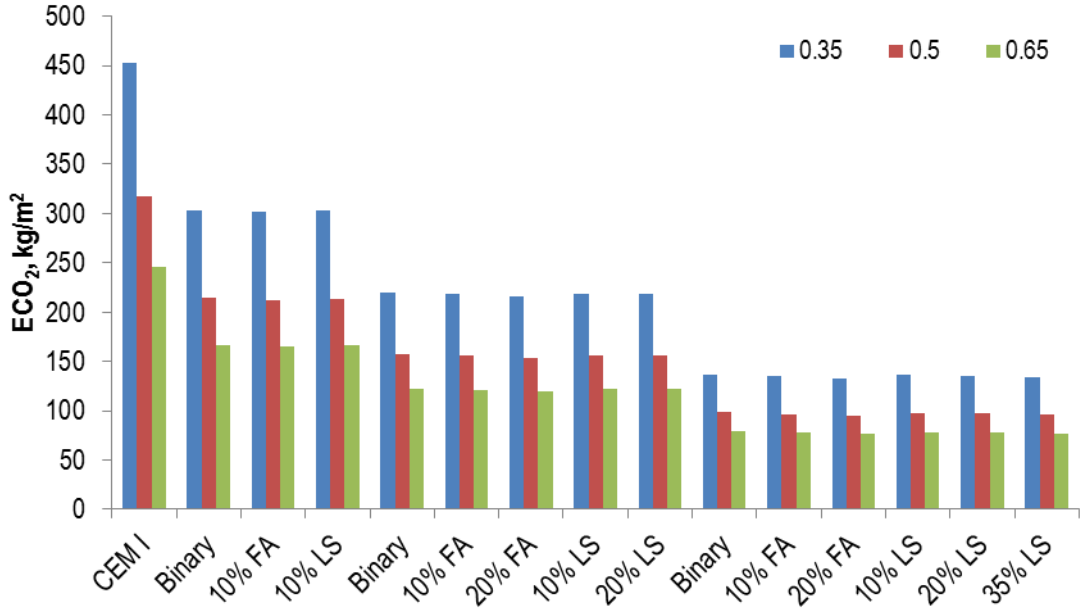


Fig 3.10: Calculated ECO_2 for all mix combinations and w/c ratios

3.13 Curve Fitting Procedure

Disparities, although being small in nature, were generally observed between individual measurements. In response to this and in aiding the interoperation of the results to a greater degree of accuracy, a curve fitting normalisation procedure was applied to the test data in this research. The steps that were followed and an example is shown in *Appendix A-5*.

3.14 Summary

This chapter has outlined the experimental programme in detail. Commencing with the material selection involving physical and chemical characterisation tests allowing for cement combinations to be formulated based on this information, the literature review and the advisement of industrial partners.

The test programme was subsequently developed to take into consideration a holistic approach to assessing the strength, permeation and durability properties of all the concrete mixes.

CHAPTER FOUR: FRESH PROPERTIES & EARLY AGE STRENGTH

4.1 Introduction

The hydration of cement paste is widely documented in the literature and to cover the full range of cement combinations and water/cement (w/c) ratios was out with the scope of this study. However, whilst it is recognised that no comparison can be directly drawn between concrete and cement paste (*Ferraris et al, 2001*) the latter can provide useful information of how materials are likely to behave in the former. A number of previous studies have concentrated on specific properties such as strength, permeability or durability and examined the effects of the fineness of cement and additions with regards to these properties to determine whether they are an advantage or disadvantage to the concrete. This study takes a more holistic approach and examines all of these beginning with the fresh properties and early strength development in this chapter.

The physical and chemical characteristics of the test materials were discussed in the previous chapter and are important in understanding their effects in cement paste, the study of which was included in order to determine the effects of additions on the reactions occurring, with regard to the changing state of the material and the development of the micro-structure.

In particular, the standard consistency and packing density, together with the setting time and yield stress were considered in order to examine the effects of additions on the cement paste. These properties were indicative of water reduction, retardation and the workability of the concrete. In addition the SP dosages of the concrete mixes are discussed with reference to the fines contents of each of the mixes. Early age strengths, up to seven days, are discussed followed by the estimated time for each combination to reach 10 N/mm^2.

4.2 Fresh Properties

A number of fresh properties were tested using cement paste including standard consistency, viscosity (rheology) and setting time. The effects of different additions on each of these properties are considered individually and together with data concerning the fresh properties of the concrete including superplasticiser (SP) dosage and slump.

4.2.1 Standard Consistency & Packing Density

The standard consistency was tested using the vicat apparatus, following the methodology discussed in the previous chapter (3.7.1), for the full range of binary and ternary mixes and the water demand is shown in Figure 4.1. The CEM I control gave a water demand of 31.8%, whilst this was not the highest; it was greater than the majority of mix combinations considered. The binary mixes at the lower GGBS level gave water demands of 28.6% (35%) and 30.2% (55%), while the higher GGBS level of 75% gave a slight increase to 30.8%, but was still lower than the CEM I control. At 90% GGBS a further increase to 32% was obtained. Essentially as the percentage of GGBS increased so did the water demand until it exceeded that of the CEM I control mix at the 90% level.

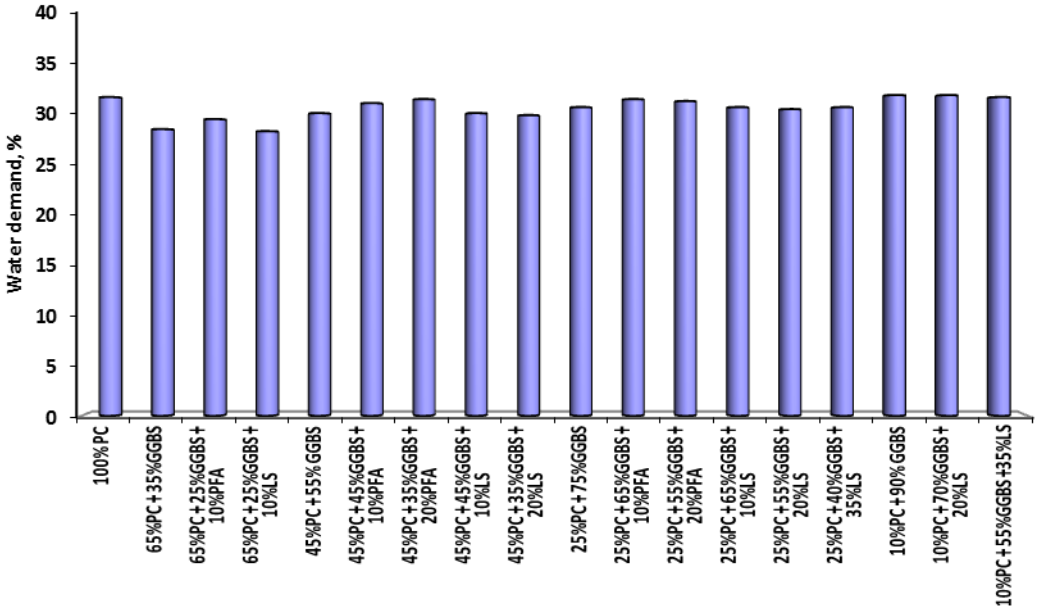


Fig 4.1: Standard consistency of paste mixes

It is widely recognised that the water demand of a paste of standard consistency will increase with the fineness of the cement or additions used (*Sivasundaram & Malhotra, 1992: Ferraris et al, 2000)* due to the increase in surface area. However, both GGBS and fly ash have water reducing properties. Indeed, Ferraris et al (*2000*) studied the effects of silica fume and ultra-fine fly ash and found that, whilst the addition of silica fume increased water demand, the fly ash had water reducing properties. GGBS tested by Lange et al (*1997*) was found to have similar effects as too did the studies on limestone cement. Vuk et al (*2001*) found that an addition of 5% limestone decreased water demand by an average of 0.5% when compared to CEM I concretes, later supported by Tsivilis et al (*2002*) where an increase of limestone content to 20% reduced water demand from 26% for the CEM I control mix to 23.5%. However, given the lack of literature for ternary blends little is known about the effects these material have when combined. In light of the studies of Sivasundaram & Malhotra (*1992*) and later Ferraris et al (*2000*), it is likely that the increase in water demand was due to the higher proportion of finer materials that create a greater surface area. These studies indicated that a higher volume of GGBS gives too many particles to adhere to the surface of the CEM I particles but at an optimum replacement level greater deflocculation occurs and a lower water demand is required, given the results of the standard consistency tests this appears to be at the 35% and 55% GGBS levels.

For the ternary mixes, a pattern emerged with the water demand increasing with the addition of fly ash. As the quantity of fly ash increased, 10 or 20% in each ternary mix, so did the water demand, possibly due to the increased carbon content of the fly ash. In contrast, the addition of limestone to ternary mixes seemed to reduce the water demand to values similar to the binary mix at each level. As the limestone doubled to 20%, the water demand decreased marginally, by 0.2%. By considering Vuk et al (*2001*), where a 5% increase in limestone decreased the water demand by 0.5%, the decrease is perhaps expected, though it is not as significant as its effect is likely to be diluted by those of the GGBS. Given that the limestone is said to be an inert filler (*Ramezanianpour et al, 2009*) its filling ability with the CEM I is more noticeable given the larger particle size of the CEM I compared to that of the GGBS. With a higher addition of GGBS the limestone has less space between the CEM I which is also being

filled by the GGBS. The limestone however, is fine enough to fit in additional spaces between the GGBS particles but with less efficiency.

Data from the standard consistency tests were used to consider the packing density of the cement pastes which were calculated using the De Larrad packing model as outlined in the previous chapter (3.7.2). The literature suggests that shape of material affects both the packing density and water demand of cement paste and in turn plays a fundamental role in obtaining a strong durable concrete (*Bentz, 1999*). The packing density of the binary mixes is shown in Figure 4.2. The lower replacement level of GGBS (35%) reduced water demand when compared to CEM I but the packing density increased. The angular shape of the GGBS may be responsible for these effects due to their ability to pack more densely than the spherical fly ash particles. The fine particles of the GGBS fill the void spaces between the larger particles and take the place of water within the pore spaces (*Wong & Kwan, 2006*).

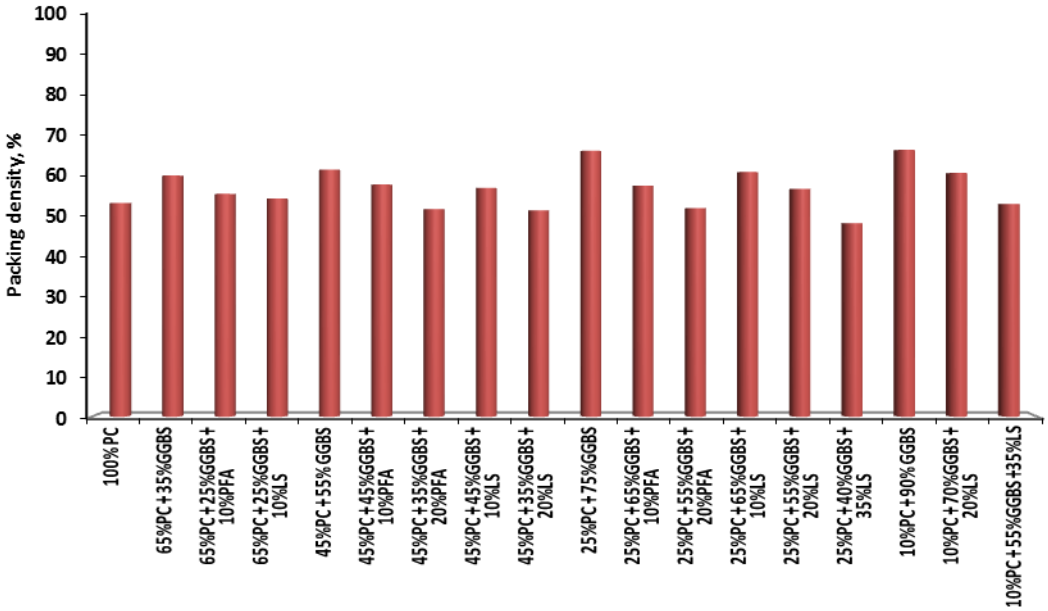


Fig 4.2:Calculated packing density of paste mixes

As the volume of GGBS increases, the angular shape of the particles enables denser packing than with the more spherical fly ash particles (*Wong & Kwan, 2006*). Indeed, as fly ash is added to create ternary blends at lower levels, the packing density decreases and the water

demand rises slightly, possibly as the voids are filled with water and not finer particles as there are insufficient quantities present to fill the voids. Had the fly ash been added in greater quantities than GGBS it might be expected that the packing density would increase further as the spherical shape of the fly ash disperses CEM I allowing the finer GGBS particles to fill the voids (*Jones et al, 2003*), but as seen in Figure 4.2 the fly ash gave a slightly lower packing density when used as a ternary addition compared to the GGBS binary at each level considered. What also must be taken into consideration is that the packing density is calculated before any inter-particle activity takes places and the dispersing effect predominantly takes place after mixing.

Overall it is GGBS that improves the packing density as a binary material. The addition of ternary material to the mix blend has a detrimental effect reducing the packing density, in some cases significantly, when compared with the corresponding binary mix. The inclusion of 10% fly ash or limestone reduces particle packing, limestone more so than fly ash as shown in Figure 4.1, although it is still slightly improved compared to the CEM I control mix at the higher GGBS level.

4.2.2 SP Dosage

Gallias et al (*2000*) note that the mineralogical, texture and granular characteristics of finer mineral additions are not taken into consideration in mix design, leading to an excess of superplasticiser being used. As discussed previously, finer materials tend to increase water demand but GGBS and fly ash can decrease this as already demonstrated in both the literature and results obtained during the study. Erdem & Kirca (*2000*) state that the higher surface area created by a binary combination, or, as in this case, ternary additions, increase water demand to maintain workability. Ferraris et al (2009) and Tsivilis et al (*2002*) indicate that a decrease in voids, or an increase in packing density, means less water required to fill the voids. Whilst the specific effects of additions have been illustrated in Figures 4.2 to 4.4, the overall influence of the fines content of the combined mix can affect their workability.

Workability can be referred to simplistically in terms of ‘high’, ‘medium’ etc., but this can lead to many differing interpretations on site (*Tattersall, 1991*). In this study, the concretes

had a fixed water content of 165 l/m^2 and equivalent consistence in accordance with BS EN 206-1 of class S2 with a nominal slump of 75± 25mm. Whilst the slump test allows for a batch to batch check of the general workability for each mix, it may not directly indicate the true workability of fresh concrete containing GGBS. The improvement in workability of GGBS concrete was not apparent in the slump test results but when vibration started the mix compacted satisfactorily in the mould.

The workability of concrete is largely determined by the content of water, or wetness of the mix process, prior to casting. The particle size distribution of the materials in the mix can also affect the workability. It can also be affected by the carbon content of certain additions such as fly ash. Overall, the cement paste combinations showed a standard consistency that was less than the lower 0.35 w/c ratio used for the concrete test mixes in the main programme. The differences ranged between 0.24 and 0.33 across the range of mix combinations and at such low w/c ratios the concrete mixes were unworkable without the addition of superplasticiser (SP). In order to attain a controlled slump, in accordance with the mixing procedure, superplasticiser was added. It was based on modified polycarboxylic ether (PCE) polymers that wrap around the surface of the cement particles during the early stage of the mix process. The result of this was a flowable concrete with a reduced water demand. With careful mix proportioning and SP dosage control, all mixes recorded a slump of 75± 10mm. The slump test is standard practice as too is the measuring of plastic density that was within range of 2390-2410mm^2.

For the binary concretes at low w/c ratio, where the fines content was high, there was little difference in the required SP dosage with varying GGBS level, that were between 0.33% and 0.35% of the cement content. As expected, an increase in w/c ratio reduced the SP dosage demand. At the lower level binary mixes, there was little difference between the CEM I and the 35% GGBS level at the 0.5 w/c ratio. However, a rise in GGBS level gave increases in the SP dosage, which were also noted at 0.65 w/c ratio. Figure 4.3 shows SP dosage in relation to the fines content of the mixes across the range of w/c ratios for the binary mixes. The fines content is calculated from the proportion of cement, additions and sand particles passing a 75μm sieve. It is evident that the inclusion of GGBS at the lower w/c ratio had a positive effect in reducing

the SP dosage. Though the decrease was small it supports the data from the standard consistency tests, indicating that less water was required for these particular mixes. When considered with the ternary additions it is clear that the inclusion of fly ash reduced the SP dosage further for both 0.35 and 0.5 w/c ratios, as shown in Figure 4.4, for the 35% addition level and Figure 4.5, for the 55% addition level.

This is contrary to the standard consistency test, which indicated a slight increase in water demand with the addition of fly ash. This suggests that the slight increase in the volume of water from 29%, to achieve a standard consistence, to 35% for the lower w/c ratio for the concrete mix, provides more water for the fly ash to react with the CEMI and GGBS to improve workability as well as better dispersal of the particles to create greater denser packing within the concrete matrix. The improvement may also be caused by the presence of aggregates, the only other differing variable between the cement paste and the concrete, however, if this were the case, it would be expected that this trend would occur throughout the range of concrete mixes. The 10% limestone addition showed signs of improvement in reducing SP dosage similar to the effects of fly ash at the lower 0.35 w/c ratio, as shown in Figure 4.4. However, unlike the fly ash ternary mix this was also reflected in the standard consistency data that gave a reduction in water demand.

At the 55% level, further improvements are seen in Figure 4.5. Given that the level of fly ash and limestone remained at 10%, it appeared that it was the volume of GGBS that caused this improvement. With regard to the ternary mixes an increase to 20% fly ash showed a further reduction in SP dosage at both 0.35 and 0.5 w/c ratios, although little further improvement was seen at 0.65 w/c ratio. These improvements, as with the 35% level, were not noted in the standard consistency data that showed an increase in water demand with fly ash level, contradicting the SP dosage demand in the concrete mixes. At this w/c ratio, the fines content is lower and the high proportion of limestone is beneficial in reducing SP dosage, and therefore water demand at this level. It is also possible however, that the standard consistence does not indicate the same behaviour as admixture demand.

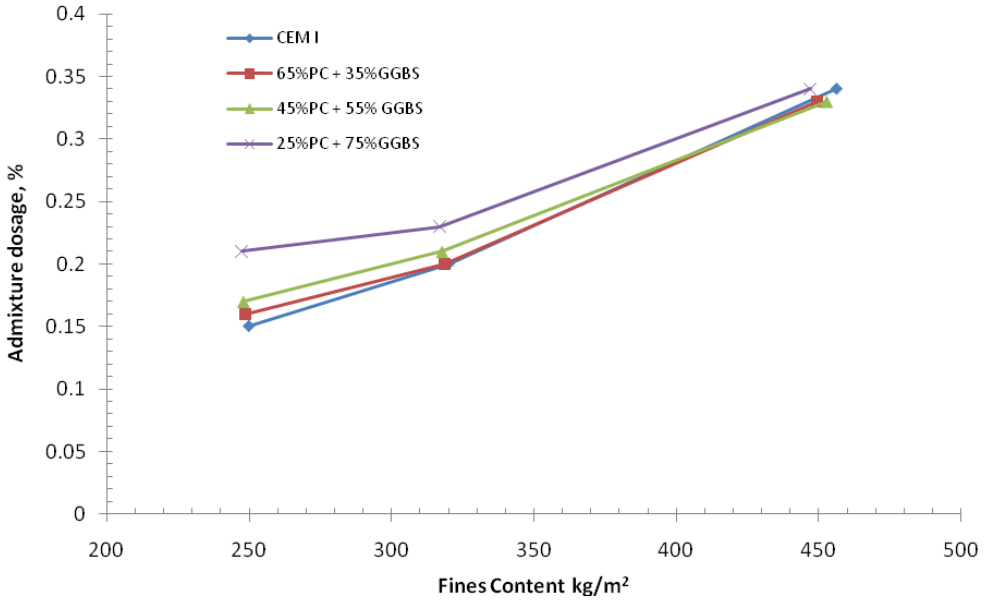


Fig 4.3: SP dosage for binary mixes across the range of w/c ratios

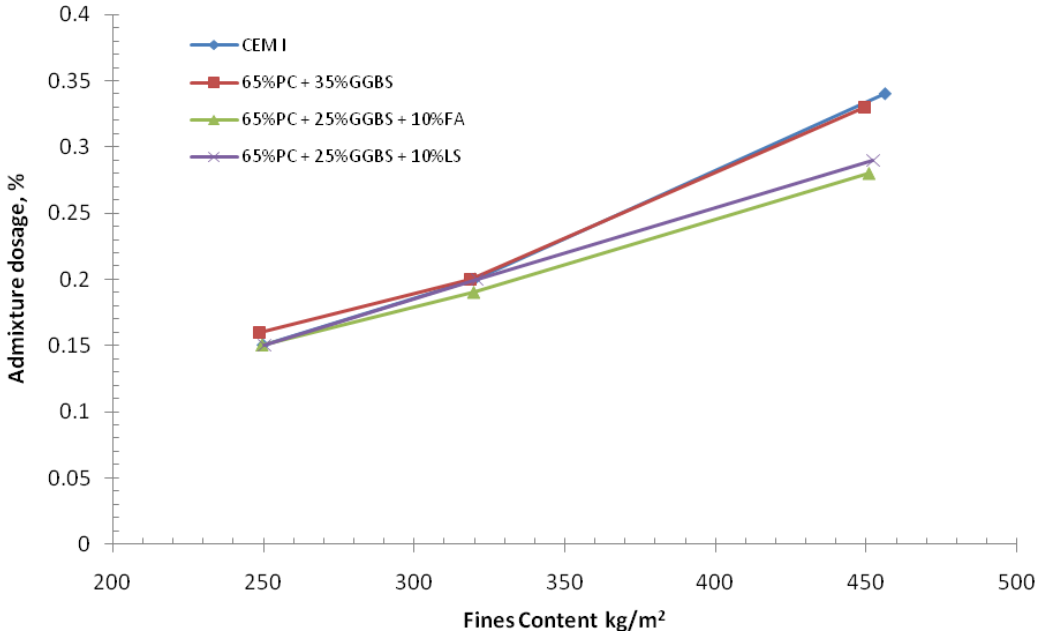


Fig 4.4: SP dosage for 35% addition level mixes across the range of w/c ratios

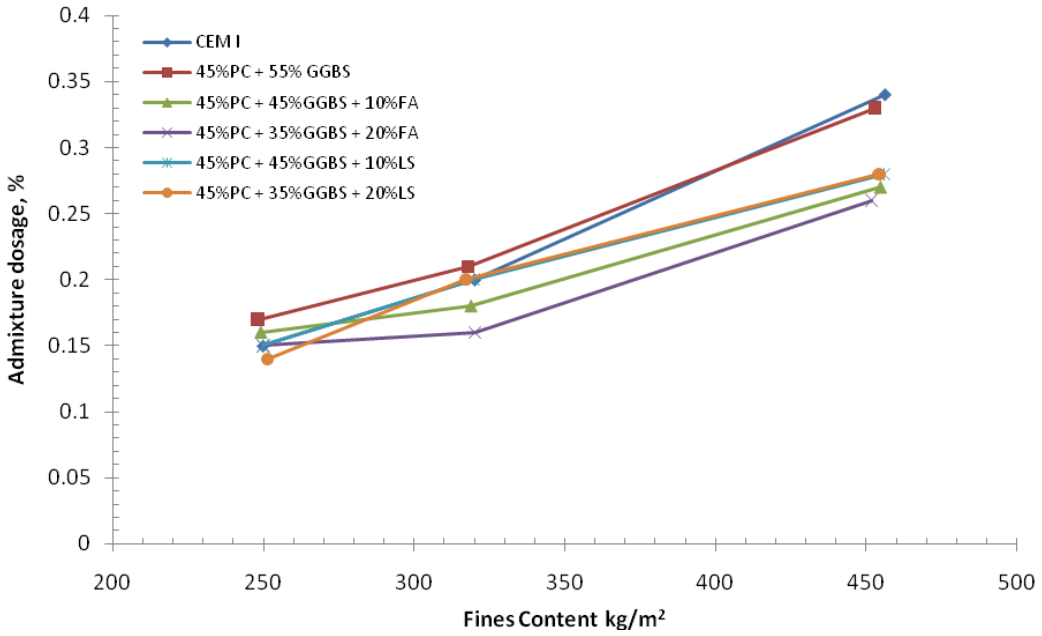


Fig 4.5: SP dosage for 55% addition level mixes across the range of w/c ratios

4.2.3 Rheology

Mindness & Young (*1981*) indicate that the water content of a mix is the single most important factor in determining workability. However, whilst an increase in water content can increase flow and compactability, it also leads to segregation and bleeding. The aim is to produce a concrete that is cohesive and the careful choice and grading of aggregates is of fundamental importance. Separation of the larger aggregates in the final mixing process can be avoided when the aggregates are combined with a cohesive cement paste, indicated by the viscosity tests. The viscosity of the cement paste would be indicative of the workability of the concrete as a higher viscosity will mitigate against segregation.

Rheology was measured using a Brookfield viscometer on the various cement combinations at 0.5w/c ratio. Data obtained from these tests were used to determine both the plastic viscosity and yield stress of these mixes. It was initially intended to carry out the same tests at 0.35 w/c ratio but the consistency of the paste did not allow the spindle of the

viscometer to move within the paste. The yield stress is shown in Figure 4.6 and the plastic viscosity in Figure 4.7. The former indicates the stress above which the concrete will become fluid and begin to flow whilst the latter indicates how easily the concrete will flow once the yield stress is overcome.

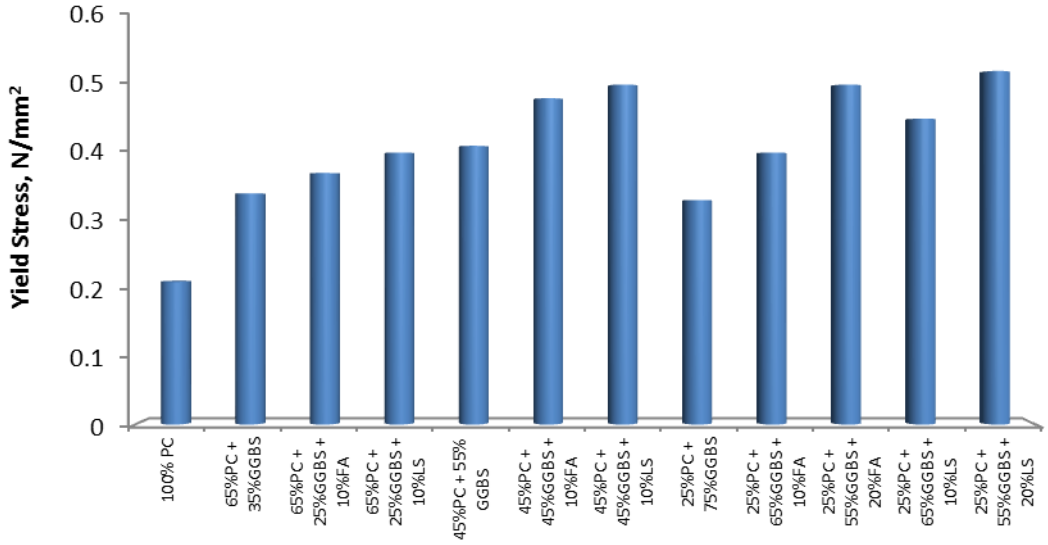


Fig 4.6: Calculated yield stress of paste mixes at 0.5 w/c ratio

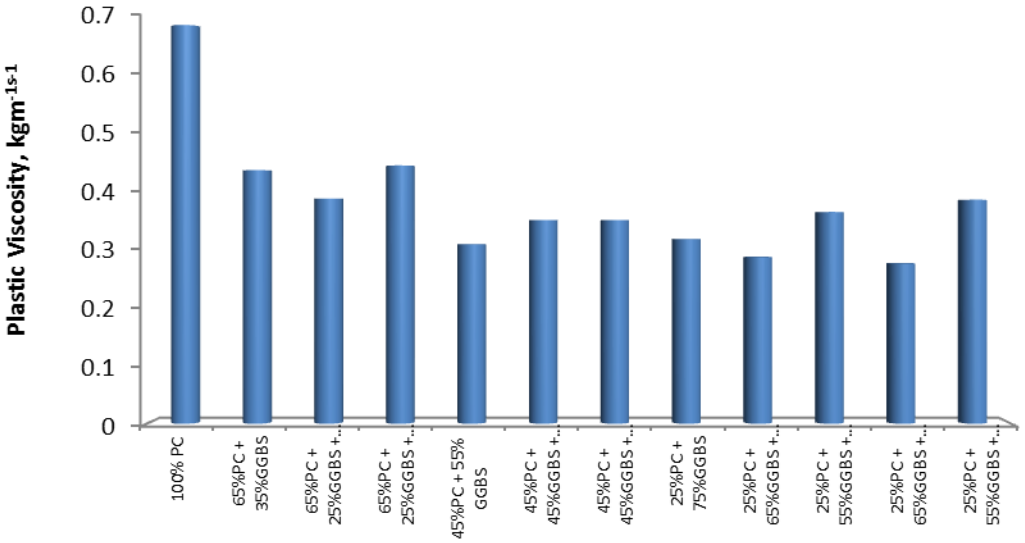


Fig 4.7: Calculated plastic viscosity of paste mixes at 0.5 w/c ratio

The CEM I control mix was calculated as the highest plastic viscosity at 0.69kgm^{-1}s^{-1}, whilst its yield stress was 0.21N/mm^2, the lowest for these mixes. The binary mix at the 35% GGBS level gave a decrease in plastic viscosity to 0.44 kgm^{-1}s^{-1}, while the limestone ternary at this level was only marginally higher at 0.45 kgm^{-1}s^{-1} whilst its fly ash counterpart was markedly lower at 0.39 kgm^{-1}s^{-1}. The yield stress at the 35% level was greater than that of the CEM I control mix, increasing to 0.34N/mm^2 for the binary and increasing further for the fly ash and limestone ternary mixes, with the latter showing the greater increase of 0.4 N/mm^2.

At the 55% level the increase in GGBS gave further increases in yield stress to 0.41 N/mm^2. The ternary blends at this level followed the same trend as 35% level, increasing the yield stress. The plastic viscosity for these mixes, however, decreased compared to the lower level. An increase in GGBS level to 75% gave similar results to those at 55% for the binary mixes, whilst the yield stress reduced. Though the structure of GGBS can vary depending on the processing this is likely to be due to the structure of the GGBS particles themselves, whilst they may appear angular in shape their surface is smooth and may allow them to move more freely.

Figure 4.8 shows the packing density against the yield stress of the tested paste samples. The packing density is calculated using the previously discussed De Larrad method based on the 0.5 w/c ratio to ensure that would be more comparative. At the lower to mid-range addition level, an increase gives no difference in particle packing compared to the CEM I control mix for the binary mixes and the limestone ternary mixes. However, the yield stress is increased with the limestone addition increasing it further. The fly ash ternaries at the 35% and 55% replacement level give comparable packing density results to that of the 75% replacement level mixes for both the binary and the two limestone ternary mixes. Indicating that the fly ash improves packing density, as previously discussed, but there is no correlation with the yield stress increasing also.

Overall the results indicate that the addition of finer materials such as GGBS increased the yield stress of the cement paste. This is further increased with the inclusion of fly ash and limestone to create ternary blends. Ferraris et al (2001) incorporated Ultra-fine Fly Ash (UFFA)

in their study with similar results. It must however be noted that the properties of the materials differ between Ferraris et al's study and this one, specifically the fineness.

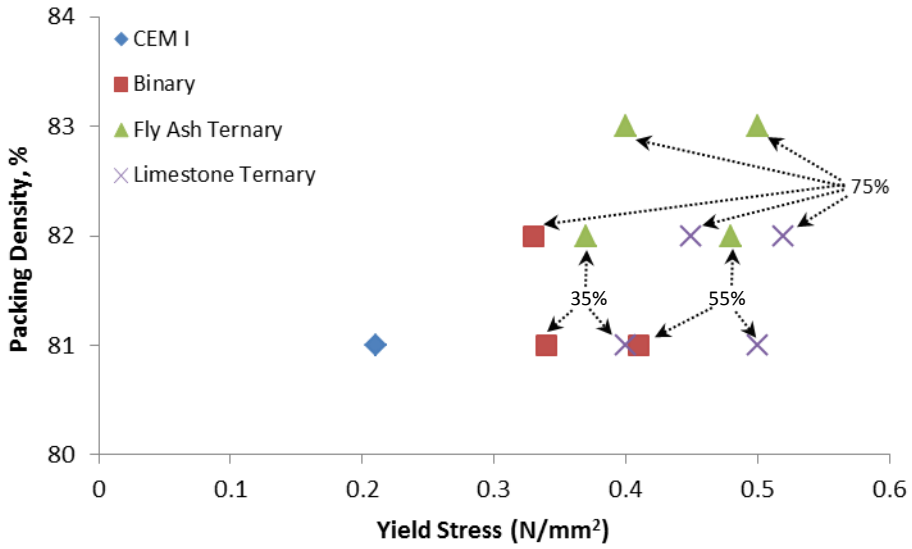


Fig 4.8: Packing density and yield stress comparison

4.2.4 Setting Time

Setting tests are used to evaluate comparative behaviour (*Sleiman et al, 2009*) assisting in characterising how particle cement pastes change state which can be affected by water/cement ratio and temperature (*Eran et al, 1995*) and the type of additions used. Realistically, in a working environment, the hardening of a concrete must not be too soon as to compromise its workability and becomes an important factor for consideration when scheduling the phases of construction (*Brooks et al, 2000*). BS EN 197-1:2000 indicates that the initial setting time for cement of strength class 42.5 N should be a minimum of 60 minutes, for higher strength cement this is reduced to 45 minutes. It should, however, be noted that the rate of setting and hardening is independent of strength gain. It is also a different property with cement paste to that of hardening in concrete (*Neville, 1995*).

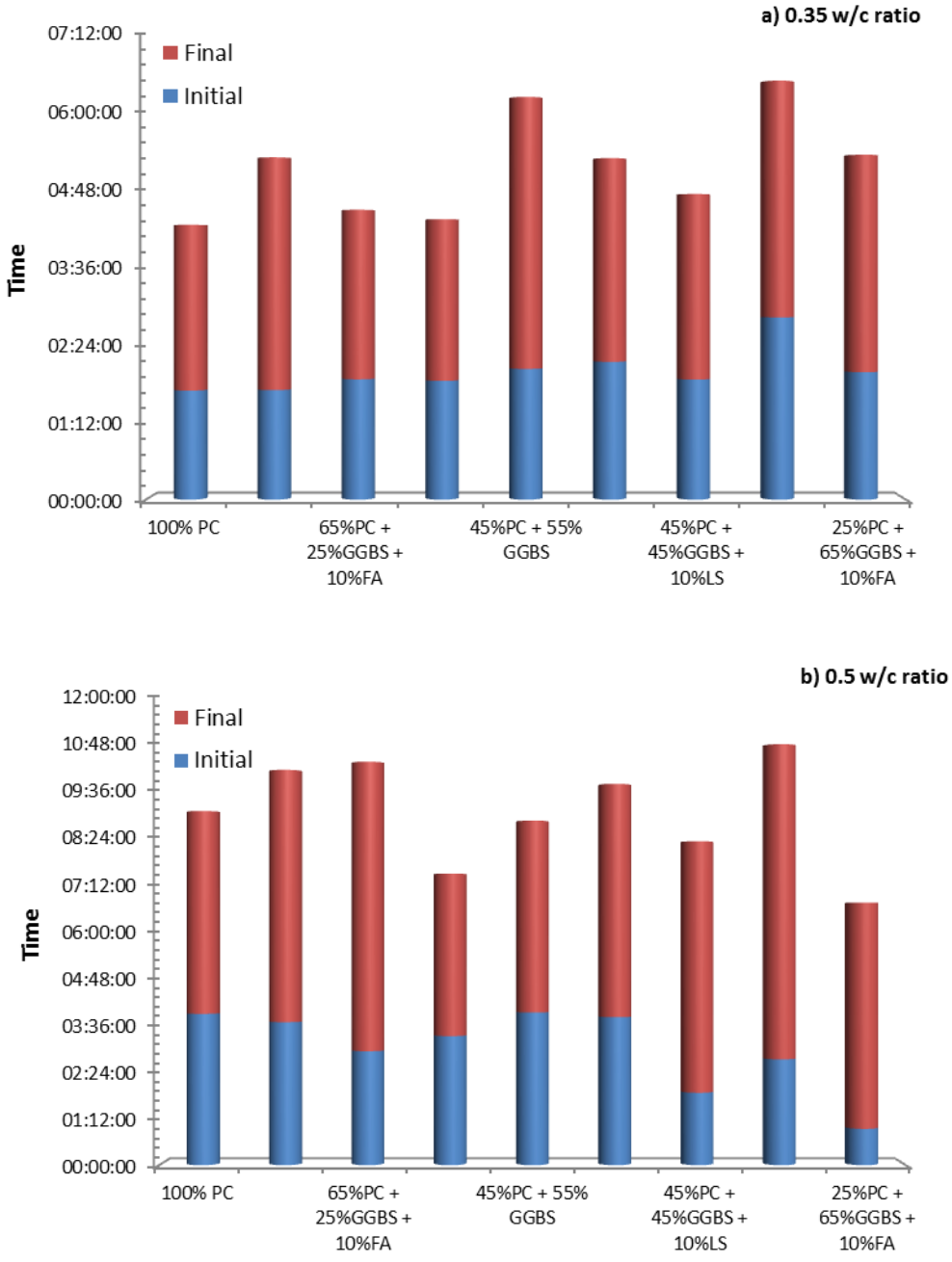


Fig 4.8: Setting time of paste mixes

Tests of setting time were carried out on selected paste mixes at both 0.35 and 0.5 w/c ratios and are shown in Figures 4.8. As expected, all mixes at 0.35 w/c ratio started to set earlier than at that of 0.5 w/c. In general, the initial setting times were comparable with the PC control mix starting at 1hr 41mins, with the ternary mixes of the 0.35 w/c ratio mixes setting within ± 10 minutes at 35% GGBS level. More significant differences were noted at 55% GGBS where the start time for both the binary mix and that incorporating 10% fly ash exceeded 2hrs. A similar increase in setting time with GGBS level was also found by Sivasundaram & Malhotra (*1992*). The binary at this level (45/55) also took the longest time to reach a final setting time of over 6 hours. The addition of 10% fly ash reduced the final setting time by just over an hour. The addition of 10% limestone at this level gave different behaviour. Indeed, its initial setting time was more comparable with the PC control, binaries and ternaries at the 35% level, taking about 4 hours to reach final setting.

Hogan & Meusel (*1981*) reported that GGBS can delay the setting time when compared to CEM I by 10 to 20 minutes for 10% addition, Yuan et al (*1984*) state that fly ash has a similar retarding effect with 20 minutes more likely for 10% addition. The retardation is caused by the delay in reaction. When the cement comes into contact with water in the first instance the dissolution of some phases takes place rapidly, the liquid phase is generally controlled by the calcium, sulfate, sodium and potassium ions in the resulting solution (*Yuan et al, 1984*). Differences in the calcium and sulfate content can alter the rate of reaction and thus the setting time. Fly ash itself has no cementitious properties until it comes into contact with water in which it chemically reacts with $Ca(OH_2)$ to form compounds that are cementitious by nature, it is activated by high alkali concentration and reacts with Ca to form gel.

With regards to GGBS, it is the CEM I that reacts initially with only a small quantity of GGBS releasing calcium and aluminium ions into the solution. The quantity of limestone at the lower replacement level counteracts the retardation effects of the GGBS resulting in reduced final setting time. $Ca(OH)_2$ is produced by the Portland cement, as a result of hydration, the addition of GGBS reduces rate of $Ca(OH)_2$ produced as it is consumed by the GGBS. Vuk et al (*2001*) discussed the effects of limestone in decreasing setting time and suggests that this is due to the C_3S content in the clinker. Low C_3S levels in the clinker were found to shorten the

setting of limestone cements by 50 minutes, whilst a higher content decreased it by only 25 minutes (*Vuk et al, 2001*). At the higher addition level, the volume of GGBS reduces the lime content. The latest setting time at 0.35 w/c ratio is that of the 75% GGBS binary mix, which did not begin to set until 2hrs and 50 mins after initial mixing. At 0.5 w/c ratio, the start time for this binary combination was comparable but the last to complete setting at 8hrs 7mins. The 45/45/10 limestone mix at 0.5 w/c ratio was comparable, to its 0.35 counterpart.

It was expected that the increase in w/c ratio to 0.5 would also increase the initial setting time. The start time for setting for the other mixes at 0.5 w/c ratio were later, all after 3hrs but given the higher water cement ratio this is not unreasonable. On the whole it would appear that the addition of GGBS extends setting time with the inclusion of 10% fly ash further increasing this at the 35%, 55% and 65% levels, more significantly at 0.5 w/c ratio. The inclusion of 10% limestone at the 35% level reduces the time elapsed between the start and finish of the setting time test but this was not consistent at the 55% level, where it markedly increased.

4.3 Early Age Strength (up to 7 days)

By comparing the data for early age strength to that of 28 day strength in Figures 4.10 (paste) and 4.11 (concrete) it was seen that for all mix combinations at the lower 0.35 w/c ratio, the strength recorded at 3 and 7 days was over 50% of the 28 day strength of each mix. This also occurred for most of the mixes at higher w/c ratio (excluding the 65/25/10 limestone, 25/65/10 fly ash and the 25/40/35 limestone). At 3 day testing the CEM I had already reached 92% of its 28 day strength, due to its quicker reaction, or hydration properties. In comparison, the paste mixes gave a higher percentage of 28 day strength at 0.35 w/c ratio, by 7 days the binary and ternary paste mixes had reached over 70% of their 28 day test results. This higher strength of the cement paste indicates the effects of the ITZ and the aggregate bond. Given that the strength of concrete is dependent on the strength of the cement matrix and its bond with the aggregate (*Poon et al, 2004*), the lower strength is indicative of the weaker phase in the development of concrete and relies on further strength development over time.

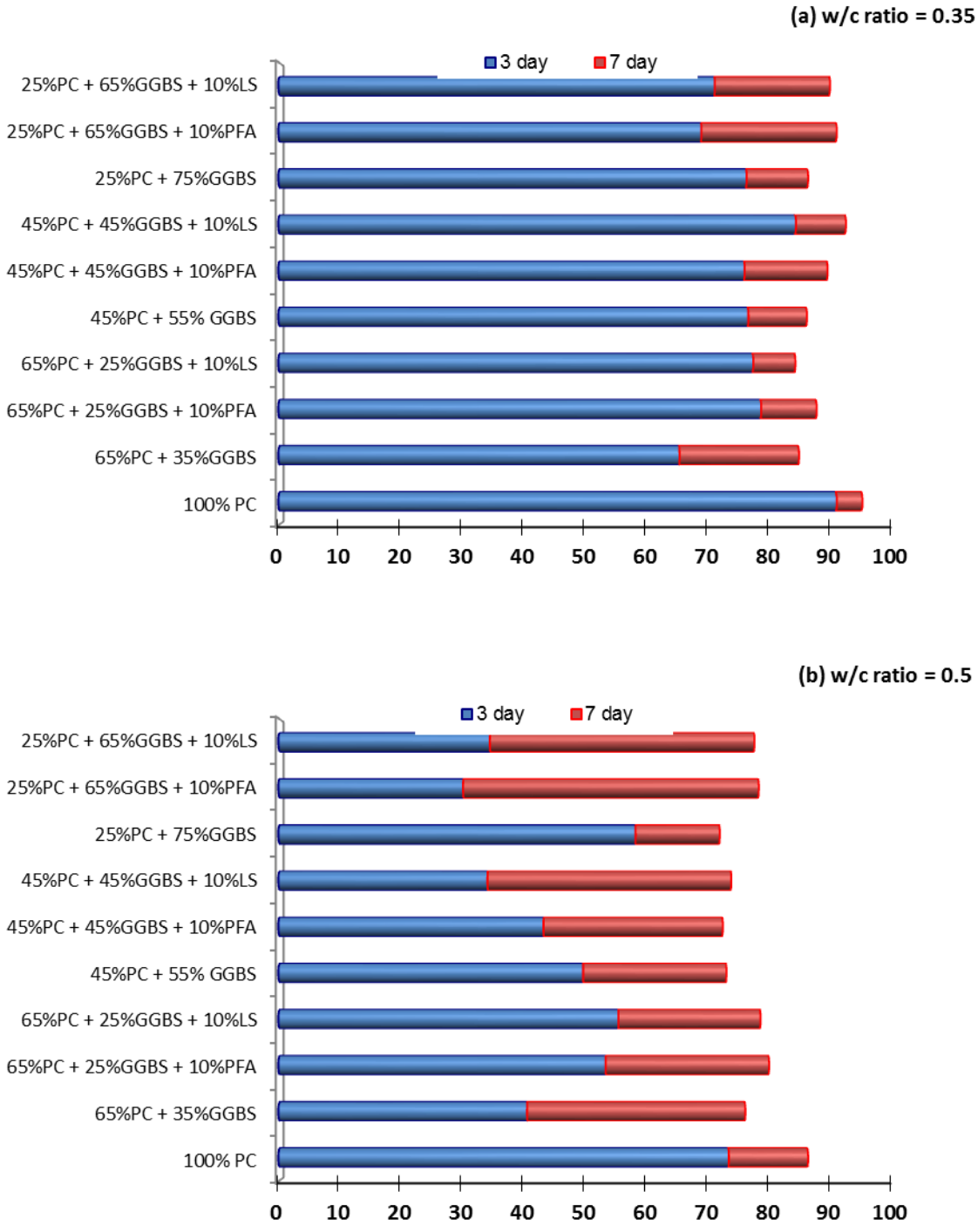


Fig 4.10: Percentage of early age paste strength compared to 28 days

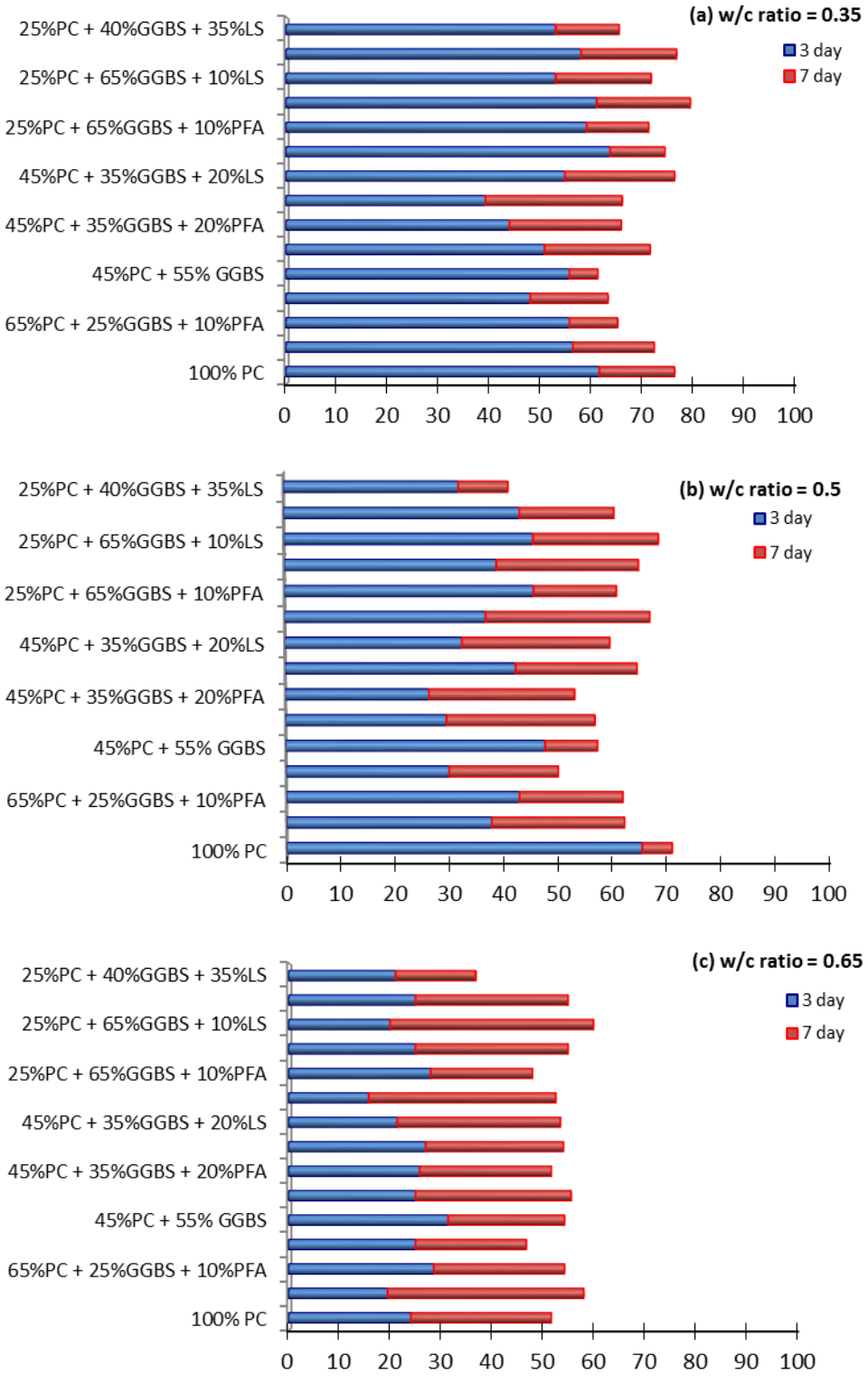


Fig 4.11: Percentage of early age concrete strength compared to 28days

Paste mixes were only tested at 0.35 and 0.5 w/c ratios. At 3 days there is a general difference range of 20-30% between mixes for both w/c ratios. The greatest difference appears when 10% limestone or fly ash is added at the higher replacement levels in 55% and 75% GGBS mixes. The mixes at the lower 35% level and all binary mixes tested, remained within a range of 22% ± 5 of CEM I. With a higher addition level for the ternary mixes (55% and 75%) there was no improvement in early age strength of the cement paste. Improvements were seen at 7 days as the strength continued to develop, where the strength of the binary and ternary mixes were almost comparable with the CEM I.

It is evident that the ternary additions have an effect on the binary mix which becomes more apparent if the w/CEM I ratio is considered at the early 3 day test age. Figure 4.12 shows the effect of the fly ash and limestone at each of the binary levels across the w/CEM I ratio range. At the lower 0.35 w/CEM I, ratio the difference in the strength across the binder ratios, as the effect of the slow hydration of GGBS becomes increasingly apparent as the volume of GGBS increases. At the lower GGBS level, where only 10% additions were used, a negative effect was observed. The additional material slows strength development further. An increase to the 55% level shows that the 10% fly ash improves early age strength marginally compared to that of the other ternaries. At the higher replacement level the positive effect of the fly ash was more evident as was an increase to 20% limestone. The strength effect of the ternary mixes incorporating 10% fly ash was consistent across the range of w/c ratios. At the higher w/c ratio 0.5, the effect of the binder ratio was less apparent and the results of the ternaries were comparable, a similar trend occurred at 0.65 w/c ratio but at a lower strength.

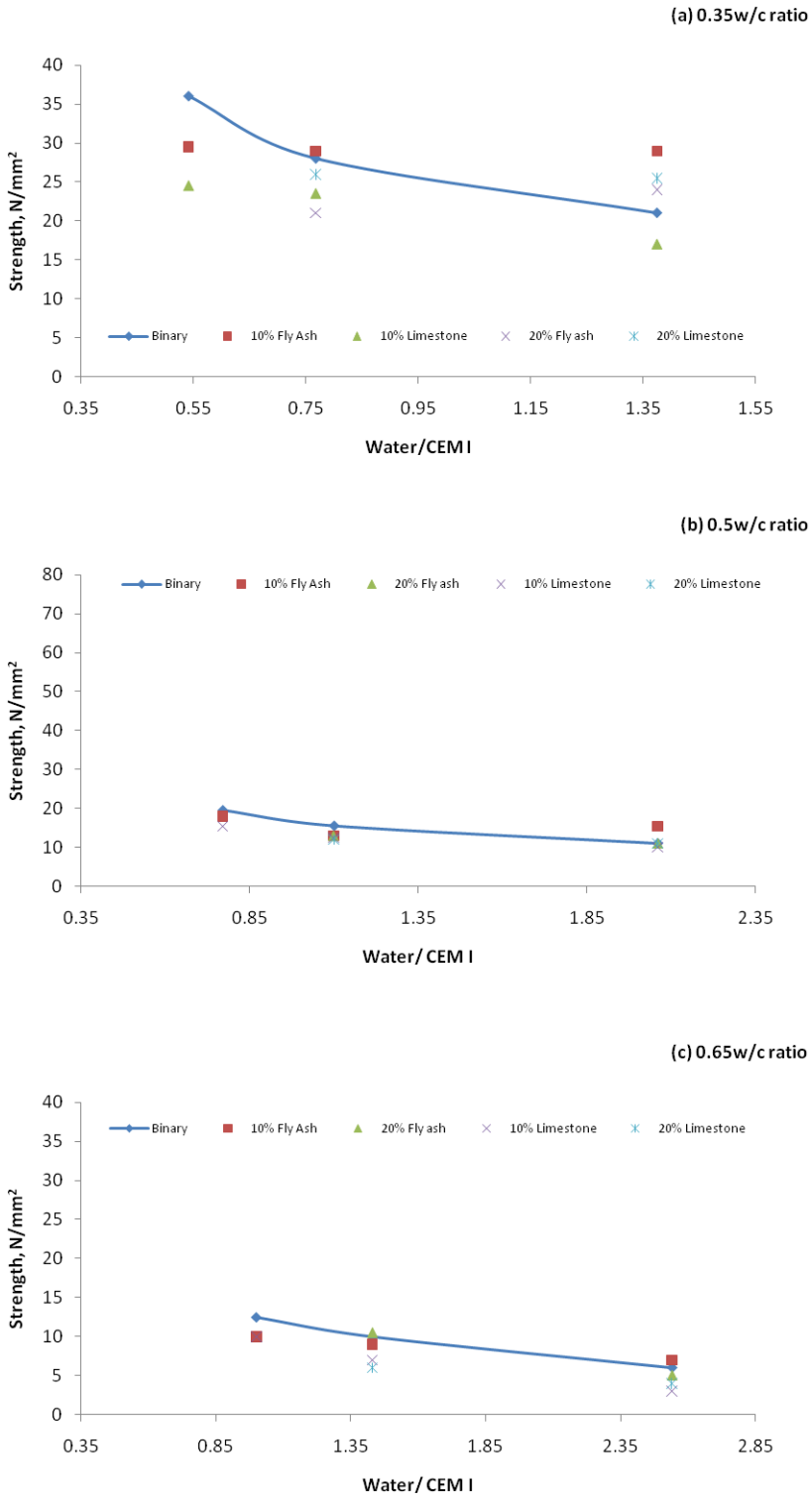


Fig 4.12: 3 day strength against water/CEM I across the range of combinations

4.4 Time to Achieve 10N/mm^2

The importance of achieving 10 N/mm^2 refers to the striking of formwork that may have to take place on site. In some circumstances this may be higher but 10 N/mm2 provides a ballpark figure for comparison that is indicative of the behaviour of concrete. Depending on the type of construction striking of formwork can be carried out any time after 12 hours or 4 days and possibly longer for slabs. The purpose of the formwork is to ensure concrete is not damaged during the vulnerable early stages and maintains its form until hardened sufficiently. It was suggested by BS 8110 (*1997*) that the formwork can be removed on site if the strength of concrete is equal, or greater than, 10 N/mm^2, if this can be predicted efficiently then construction phases may be better planned. By using a logarithmic scale the time it takes each mix to achieve 10N/mm^2 can be estimated and this is shown in Table 4.1.

Table 4.1: Estimated time to achieve 10N/mm² strength

	Expected time to achieve 10N/mm² Strength					
	Days			**Hours**		
Combination	**0.35**	**0.50**	**0.65**	**0.35**	**0.50**	**0.65**
100% PC	0.20	0.34	0.74	4.80	8.10	17.70
65%PC + 35%GGBS	0.26	0.57	1.52	6.20	13.70	36.50
65%PC + 25%GGBS + 10%FA	0.32	0.66	3.00	7.60	15.90	72.00
65%PC + 25%GGBS + 10%LS	0.31	0.90	3.00	7.50	21.50	72.00
45%PC + 55% GGBS	0.34	0.97	3.15	8.10	23.20	75.70
45%PC + 45%GGBS + 10%FA	0.32	1.37	3.24	7.80	32.80	77.80
45%PC + 35%GGBS + 20%FA	0.51	1.37	3.00	12.10	32.80	72.00
45%PC + 45%GGBS + 10%LS	0.43	1.52	3.87	10.20	36.50	92.80
45%PC + 35%GGBS + 20%LS	0.40	1.70	4.47	9.60	40.80	107.30
25%PC + 75%GGBS	0.51	2.20	4.92	12.10	52.90	118.00
25%PC + 65%GGBS + 10%FA	0.32	0.90	4.99	7.80	21.50	119.70
25%PC + 55%GGBS + 20%FA	0.41	2.20	5.49	9.90	52.90	131.90
25%PC + 55%GGBS + 20%LS	0.84	3.98	7.94	20.10	95.50	190.60
25%PC + 40%GGBS + 35%LS	0.74	4.58	8.32	17.70	110.00	199.80

It must be stressed, however, that these times shown in Table 4.1, are only an estimate and whilst previous studies have used this method to extrapolate data it may be argued that this is not a true representation of the development of strength in the early stages. It may well be that the initial reaction of the GGBS causes a sudden, quicker increase before slowing in the first few hours. In addition, whilst it is important to ascertain the strength of concrete, in general, laboratory testing cannot provide a true representation of the environmental effects that in situ concrete may endure. Such tests do not accurately reflect the strength development of in situ concrete that is affected by a number of variables such as thickness of slab, binder content and temperature. The purpose here is to provide a comparison between the concrete.

Formwork is extensively used, creating further restrictions on the management of construction projects and BS 8110 (*1997*) and CIRIA Report 136 (*2004*) lay out specific guidelines on the striking of formwork in order to ensure a good sound structure. The formwork protects the concrete during the early stages from damage and weather elements. The standard recommends 4 days for the soffit formwork to slabs and 12hrs for vertical formwork at an ambient temperature of 16^{o}C. Shorter periods are acceptable for slabs and beams only if their strength is equal to, or greater than 10 N/mm^2 in situ, or twice the stress to which they are being subjected (10 N/mm^2 is usually the greater of these) 5N/mm^2 is acceptable for members in compression to protect against frost damage. Should, however, the slab be less than 250mm in depth and have a length of at least 7.5m shorter periods than 4 days are not allowable. With this is mind it is evident that all mixes for 0.35 and 0.5 w/c ratio were suitable when the time to 10N/mm^2 is assumed to follow a logarithmic scale as is suggested by Li & Zhao (*2002*). It must be remembered that this is hypothetical in this instance and may not necessarily be the case but the test result for 3 days exceeded 10N/mm^2 for all these mixes and therefore definitely conformed to the 4 day restriction. It may be possible that early strength development of concrete does not follow a logarithmic scale but gives a rapid growth during the initial 24 hours, further tests would need to be carried out in a separate study and would be needed to take place to confirm this before a decision is made as to the best combination for vertical formwork requiring 12 hours to reach 10N/mm^2. The British standard recommendations are irrespective of binder type and a later report produced by

CIRIA (*CIRIA Report 136, 2004*) provides tables for CEM I strength classes 42.5 and 52.5 only and does not include materials such as GGBS or fly ash. Whilst the former ultimately provides high strength at a later age it is recognised that incorporating GGBS with CEM I to provide a binary blended concrete causes slower early age strength development which is clearly indicated in Figures 4.13 to 4.15. In spite of this, however, a report by the Institution of Civil Engineers (*1994*) on "Formwork Setting Times for GGBS Concretes" stated that *"where only up to 50% GGBS is used; the reduction in early age strength development has not presented problems significant enough to prompt much field investigation."*

It has been well documented in previous studies that the effect of adding GGBS, and indeed fly ash, whilst contributing to greater long-term strength development of concrete, depresses early age strength. Despite delayed setting times, allowing for longer periods of workability and a greater viscosity, requiring less energy for movement allowing for flowable and easy placement of concrete, GGBS reacts at a slower rate, causing slower early age strength gain. This can lead to problems with accelerated construction schedules when striking of formwork at the earliest and safest convenience is important. Early studies assumed that the early strength development of concretes followed a logarithmic relationship (*Gonnermann & Lerch, 1951; United States Bureau of Reclamation, 1975*). It is therefore possible, by using the early age strength data; to extrapolate the time it takes for each mix to achieve 10 N/mm^2. Li & Zhao (*2002*) also used a logarithmic scale to illustrate their strength data as described previously in Chapter 2.

At the 35% GGBS level, the binary mix took longer than the CEM I control across the range of w/c ratios. The addition of 10% limestone or fly ash, to create ternary mixes, further increased the time to achieve 10N/mm^2. At the 0.35 w/c ratio the results are comparable but at 0.5 w/c ratio, the limestone gave an increase of nearly 6 hrs. At the higher w/c ratio again fly ash and limestone results were comparable.

An increase in GGBS replacement to 55% also increased the time to achieve 10 N/mm^2 by 1.9hrs compared to 35% and 3.3hrs compared to CEM I at the 0.35 w/c ratio. As is the trend across the range of w/c ratios the time to achieve 10 N/mm^2 is increased, on occasion

considerably, taking just 8.1hrs at 0.35 w/c ratio to 75.7hrs at the higher 0.65 w/c ratio. The addition of 10% limestone did not improve the results, increasing the time further across the range of w/c ratios. At 0.35 w/c ratio however, a slight decrease was recorded when 10% fly ash was added. This was very slight and practically insignificant, at only 0.3hrs and only seen at this w/c ratio, for others the time increased for the binary mix, but remained lower than the 10% limestone.

At the 55% level, 20% ternary additions were also tested. Increasing the fly ash to 20% also increased the time to achieve 10 N/mm^2 by 4 hours at the lower w/c ratio. The mid-range fly ash results were comparable whilst at 0.65 w/c ratio the 20% fly ash had decreased by 6 hours. A decrease was also noted with the increase from 10% to 20% limestone at the lower w/c ratio; it was however, negligible at less than 45 minutes. An increase in w/c ratio increased the time to achieve 10 N/mm^2 further.

At the 75% level, a 35% limestone ternary was introduced. The initial strength development of this mix was similar to that of the 10% limestone, whilst the 20% ternary reacted quicker which seemed to be the case across the three w/c ratios. The 10% fly ash mix was comparable to the binary mix at the lower 0.35 w/c ratio, an increase to 0.5 w/c ratio showed a better initial reaction for the 10% fly ash and a further increase to 0.65 w/c ratio gives comparable results to the CEM I. Greater difference in the reaction was seen at 0.35 w/c ratio and 0.5, the higher 0.65 w/c ratio has a much slower effect on strength development.

Unless the laboratory testing procedure can replicate the conditions of in situ concrete differences will remain. One of the easiest variables to control is the temperature during the curing process and unless this is controlled during curing differences will definitely occur between cube strengths and in situ concrete, yet this itself is not controllable for in situ concrete which can cure in temperatures exceeding 20^oC and indeed, far below during winter months. GGBS concretes are more sensitive to temperatures that CEM I concrete in that an increase in temperature can improve the early age strength gain. An increase in curing temperature to 40^oC can increase this strength gain by a factor of 2 of 4 making GGBS

concretes suitable for fast track construction and in many cases heat beds are used to encourage and accelerate early age strength gain (*Barnett et al, 1995*).

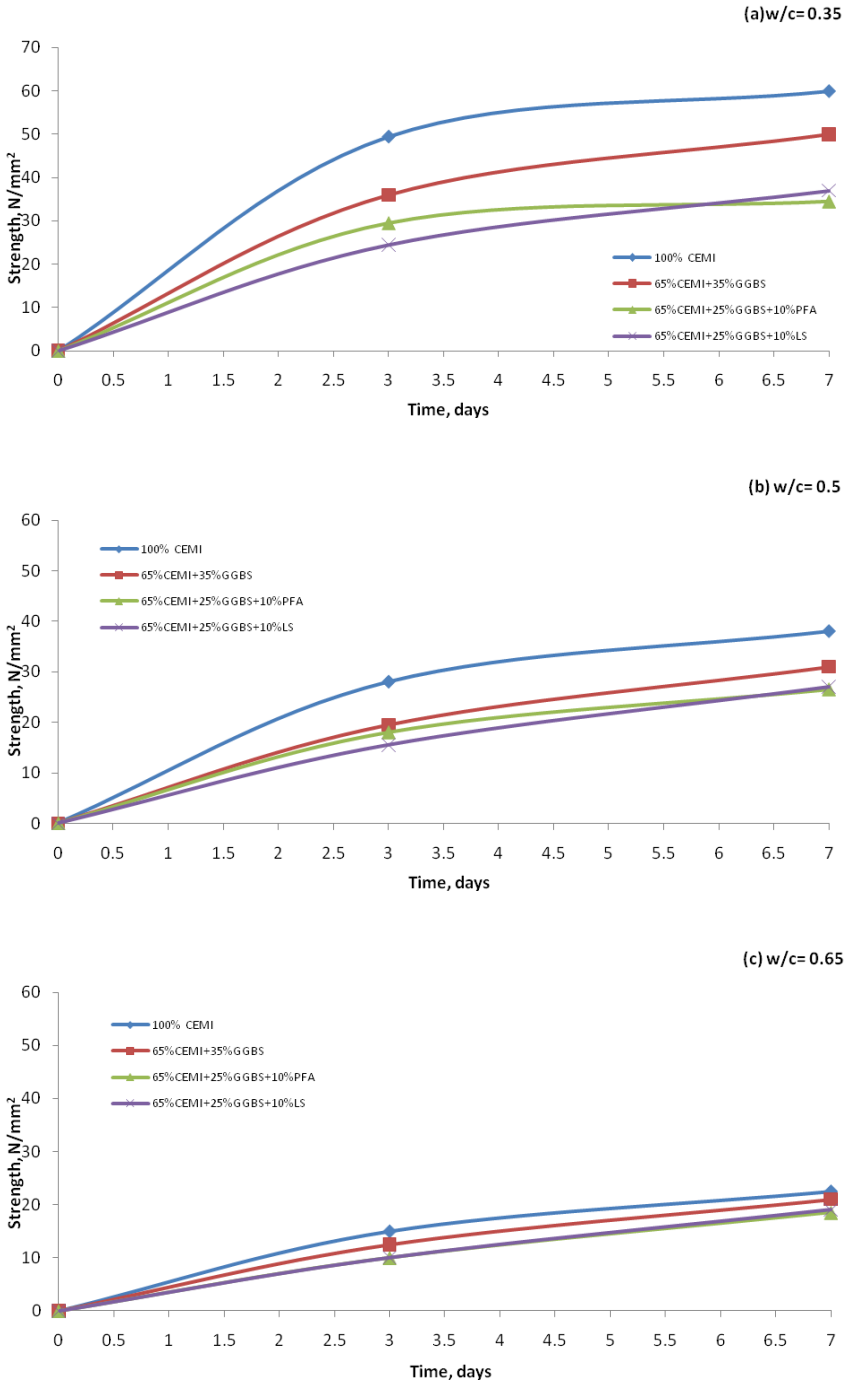


Fig 4.13: Early age strength of concrete at 35% level

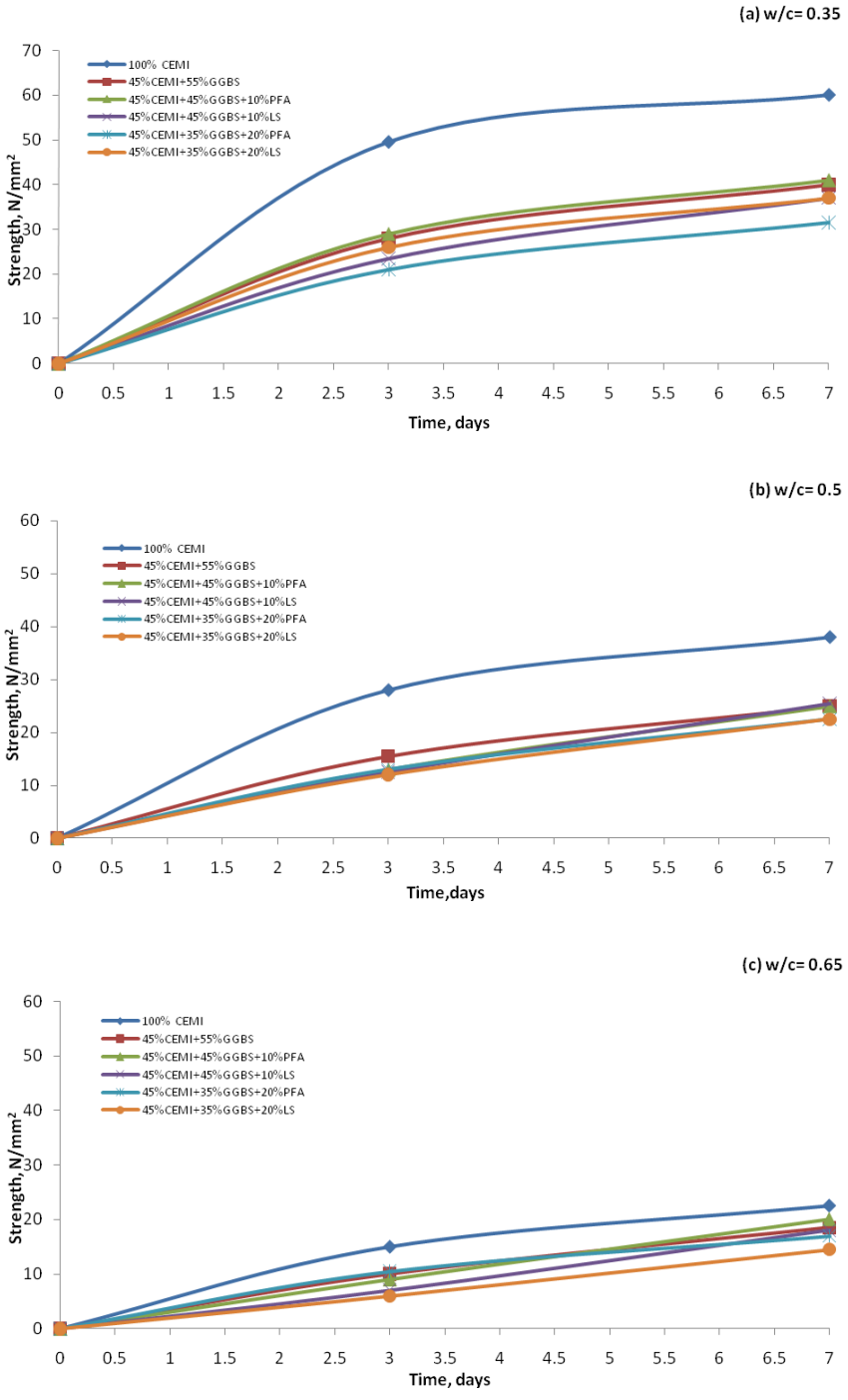


Fig 4.14: Early age strength of concrete at 55% level

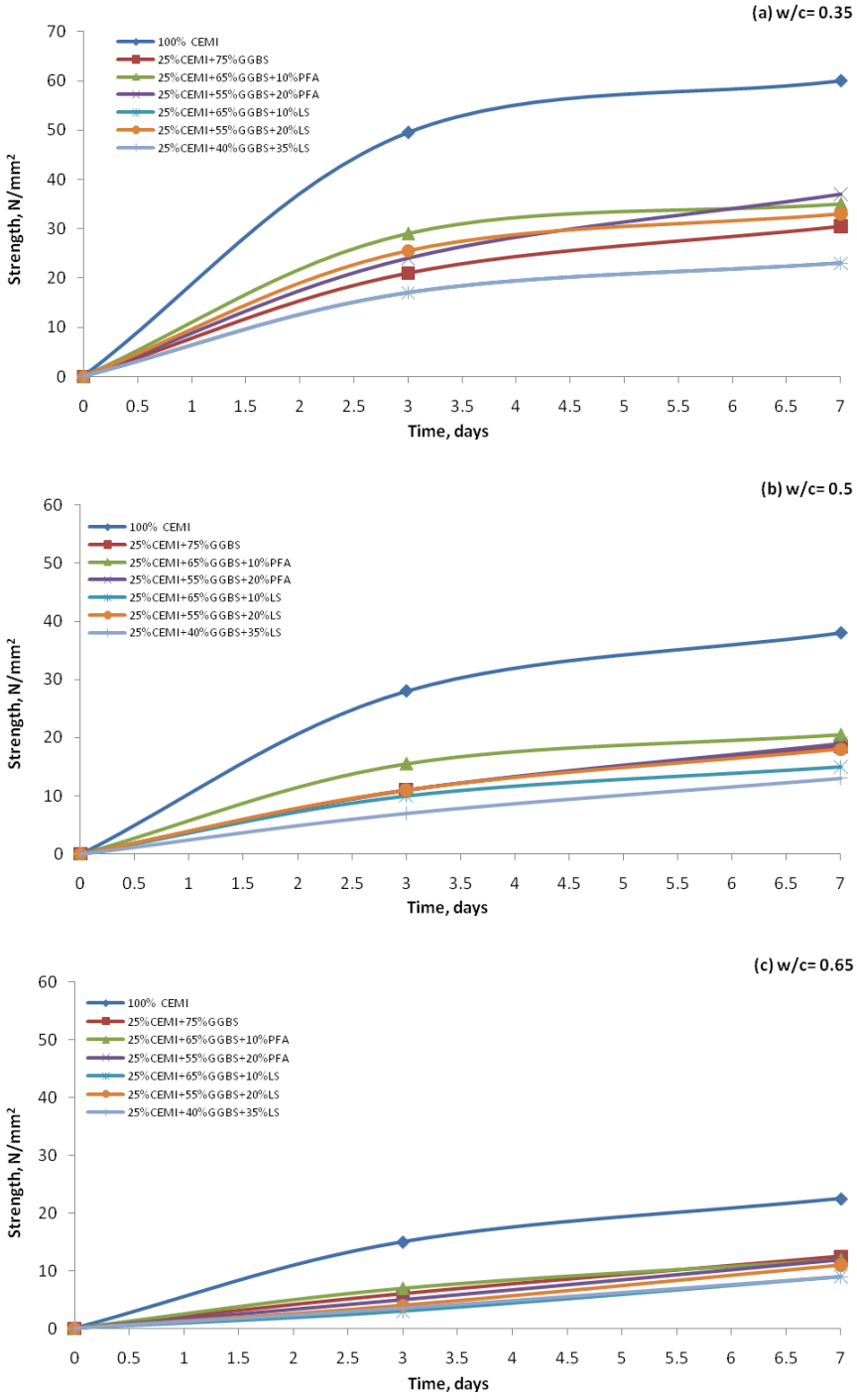


Fig 4.15: Early age strength of concrete at 75% level

4.5 Summary

This chapter examined the fresh and early age strength properties of both cement paste and concrete combinations. From the paste mixes it was seen that water demand was reduced for the binary mixes, compared to the CEM I. Whilst the addition of fly ash had the effect of increasing water demand slightly, the limestone ternary mixes reduced it further compared to their fly ash counterparts. This is supported by earlier work carried out by Vuk et al (*2001*) that showed similar effects. The packing density was also improved for the binary mixes.

A decrease in w/c ratio required an increase in SP dosage, which was not unexpected, and varying dosages were required with differing cement additions. At the 0.35 w/c ratio a very slight decrease in fines content, due to the cement additions, resulted in an increase in SP dosage with increasing GGBS level for the binary mixes. Similar effects occurred at 0.5 and 0.65 w/c ratio but the range of SP dosage was less as this was increased. The addition of ternary materials had the effect of reducing the SP dosage further across the range of GGBS levels and this was more noticeable for the 0.65 w/c ratio concretes.

Yield stress, overall, increased with the inclusion of the finer GGBS for the binary mixes. The inclusion of ternary additions increased the yield stress further with the limestone producing higher yield stress than their fly ash counterparts across the range of GGBS levels.

The setting times of the tested paste mixes increased with w/c ratio. The setting times of the binary mixes also increased with rising GGBS levels compared to the CEM I. At the lower w/c ratio the addition of fly ash and limestone reduced the setting compared to the binary mixes. However, an increase to 0.5 w/c ratio saw the fly ash ternary mixes increasing the setting time further. The fly ash had a retarding effect that was exacerbated at high w/c ratio.

It was clear that the fly ash and limestone addition affected the early strength development of concrete. At the lower w/c ratio for the lower level of GGBS this effect was negative but with an increase in GGBS level the effects were generally more positive. Increasing the w/c ratio to 0.5 and 0.65 reduced the effects that were seen at 0.35 w/c ratio.

In addition to the early age strength the time to 10 N/mm^2 was also discussed. In relation to the construction process knowledge of this can assist in reducing construction time by striking formwork at the most appropriate time so as to destroy the surface of the concrete. The time to 10 N/mm^2 was calculated and it was determined that by increasing the GGBS level the time for concrete to reach 10 N/mm^2 extends compared to CEM I concretes. The time was further increased by rising w/c ratios where less of a difference in the rate of strength development was seen across the range of mixes. The addition of ternary materials on the whole had no improvement at the 35% level and negligible improvement at the 55% level. For the 75% level, however, the initial strength development of the fly ash ternary concretes was noticeably greater that the binary at the 0.35 w/c ratio.

CHAPTER FIVE: COMPRESSIVE STRENGTH

5.1 Introduction

The strength of concrete is generally attributed to the calcium silicate hydrates (CSH) produced during the reactions of the cementitious materials with water. With a CEM I/GGBS binary mix the CEM I initially hydrates when water is added, with only a minor reaction from GGBS (*Ogawa et al, 1980*). The GGBS reacts at a later stage with alkali hydroxide and then calcium hydroxide produced by the CEM I, giving the GGBS binary concretes potential for longer-term strength development. Both Muira & Iwaki (*2000*) and Aldea et al (*2000*) discussed the two-stage reaction, but a number of factors affect the strength of concrete including, the w/c ratio, the soundness of the aggregate, and its bond with the cement paste, and the glass content (*Tanaka et al 1983*), as well as the chemical and physical properties of the material (*Roy, 1983*).

The previous chapter discussed the fresh properties of cement combinations, both in paste and concrete, before reviewing the early age strength (up to 7 days). It was noted that the strength development for most mixes reached 50% of the 28 day strength by 7 days. This chapter continues to examine strength development of concrete, considering behaviour up to 180 days, together with the environmental performance of the concretes with regard to their embodied CO_2.

Data obtained from the strength tests is then used to determine the binder cementing efficiency. The required w/c ratio for each combination in order to attain an equivalent strength of 40 N/mm^2 is also determined. The widely reported effects of GGBS discussed in the literature review (Chapter 2) were evident, as seen from the reported data. Indeed, the inclusion of GGBS decreased water demand and increased long-term strength gain overall for the binary mixes. As these are extensively covered in previous studies, it is the effects of the fly ash and limestone additions, creating ternary mixes that are of key interest here.

5.2 Compressive Strength

A 100% CEM I control mix was used to provide a benchmark against which the binary and ternary mixes could be compared. It is well established that the addition of GGBS to Portland cement causes a long-term strength gain (*Hogan & Meusel, 1981; Roy, 1987*). This is due to the lower lime content of GGBS blended cements causing an initial slow hydration and the production of more C-S-H as a result of the reaction, resulting in a denser microstructure in the long-term. When combined with CEM I it is this material that begins to hydrate first, releasing calcium hydroxides that react with the GGBS, to form C-S-H (*ACI, 1994*). Whilst there are similarities in the chemical composition of cement and GGBS it is the higher silica content and lower calcium content of the GGBS that is generally responsible for the hydration process. The initial reaction that takes place leaves a coating on the surface of the finer slag particles delaying both the dissolution of ions and further hydration (*Detweiler et al, 1996*). *Babu and Kumar* (2000) evaluate the efficiency of the GGBS in cement in detail by comparing their strength to that of Portland cement concretes.

5.2.1 35% GGBS Level

The results in Figure 5.1 show that at 0.35 w/c ratio and 35% GGBS level the ternary mixes had considerably lower strength than the control mix at early ages. The binary mix at this level however, had comparable strength to the CEM I control. A similar result was reported by *Swamy & Boukini* (1990) who suggested that comparable strength can be produced with correct mix proportioning. They stated that by using GGBS with a relatively low specific surface area, concretes can be produced with a compressive strength that is comparable to Portland cement by 28 days, but this combined with their coarser particle size distribution does not contribute to early strength. Wan et al (*2004*) also state that compressive strength can increase with the surface area of GGBS. By 28 days, the strength of the binary mix began to pass the CEM I control. Both ternary blends, with the addition of 10% fly ash and limestone (at 0.35 w/c ratio), gave a significant decrease in strength of almost 20N/mm^2, when compared to the control mix, across the test ages 28 to 180 days. *Ramezanianpour et al* (*2009*) tested a number of mixes containing limestone and found that at a water/binder ratio of 0.37, a 10% limestone addition gave comparable results to the CEM I control mix at the early test ages, but gave slightly lower results at 28 days and suggested that this is likely to be due to the precipitate of

calcium carboaluminate hydrates, that may form during hydration, and the acceleration of hydration due to the effects of calcium carbonate ($CaCO_3$) (*Pera et al, 1999*).

At 0.5 w/c ratio, the trend of binary mixes was similar to that at lower w/c ratio at 90 and 180 days, with the strength of the binary mix giving similar or increasing strength in comparison to the CEM I control. In this case, the ternary concretes were closer to those of both the CEM I control and binary than that of the lower 0.35 w/c ratio.

An increase in w/c ratio to 0.65 had the effect of reducing the compressive strength results across the range of concretes at this addition level, including the CEM I control. By 28 days, the binary mix gave slight increases and this was greater at later test ages of 90 and 180 days than CEM I. The ternary concretes followed a similar pattern to that of the binary and showed a marked increase at ages 90 and 180 days and comparable strengths to the CEM I and binary mix at 28 days. The concrete with 10% fly ash gave the better results at this higher w/c ratio suggesting that whilst the water to cementitious material volume is higher it is adverse to the compressive strength of CEM I concrete it is beneficial to the reaction of the additional material. The materials behaved more efficiently in terms of their reactions at these lower levels. The overall strength of concrete made with a higher w/c ratio is lower as water not consumed by the reaction of the materials remains in the pore spaces due to the lack of C-S-H bonds, however the addition of GGBS and fly ash prolongs the reaction, thus increasing the production of C-S-H bonds, over time reducing the space filled with excess water.

5.2.2 55% GGBS Level

The results for this GGBS level are shown in Figure 5.2. Unlike at 35% GGBS the binary (45% PC and 55% GGBS) mix at 0.35 w/c ratio had markedly lower strength than that of the CEM I control mix at all ages. The addition of 10% fly ash and limestone gave similar behaviour from 3 to 180 days. Whilst being comparable from 3 to 28 days, these concretes gave considerably lower strength than those of the binary at 90 and 180 days. When compared to the corresponding concretes at the 10% level the introduction of 20% fly ash and limestone had little effect on strength at 0.35 w/c ratio.

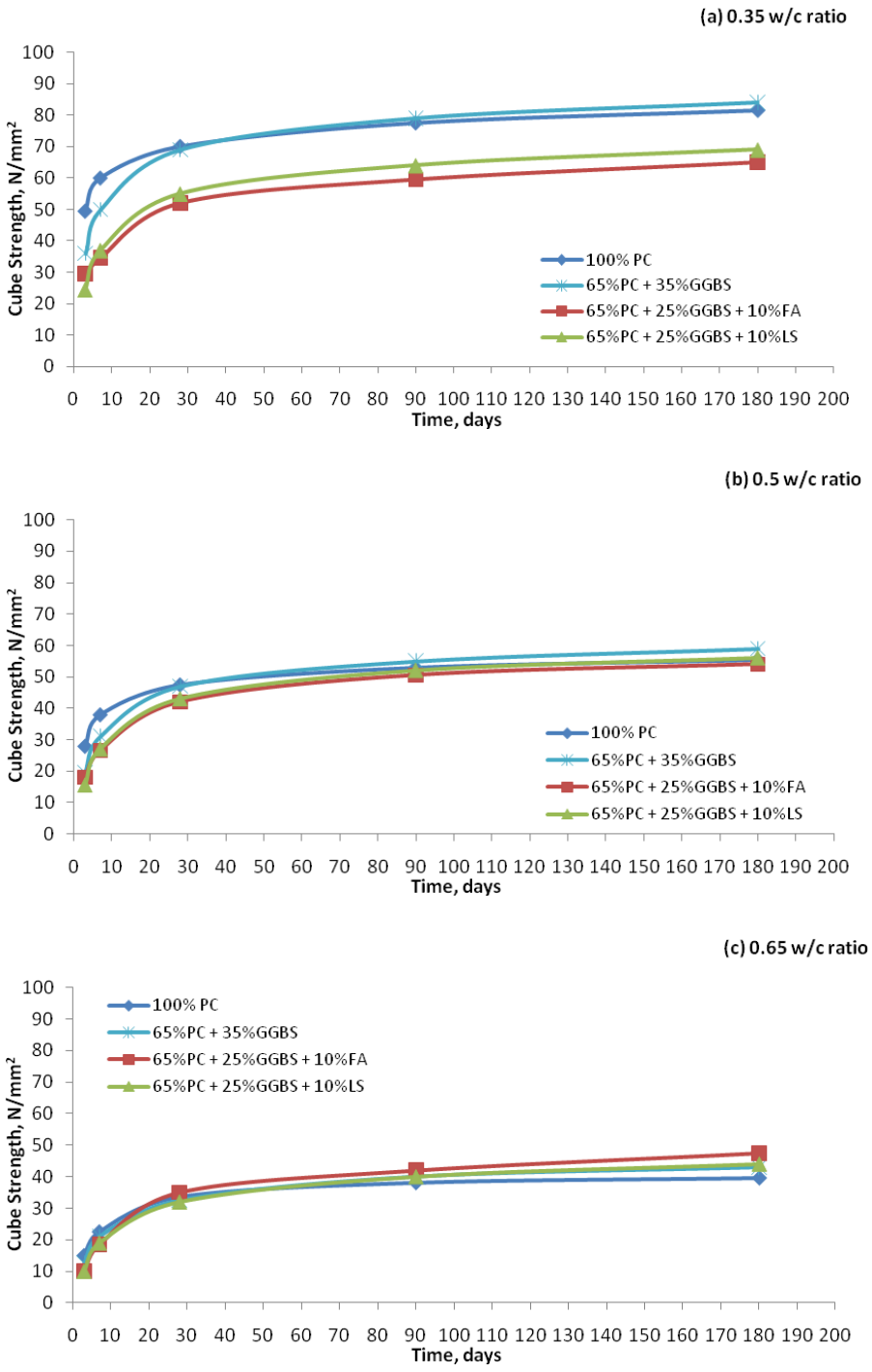


Fig 5.1: Compressive strength at 35% addition level

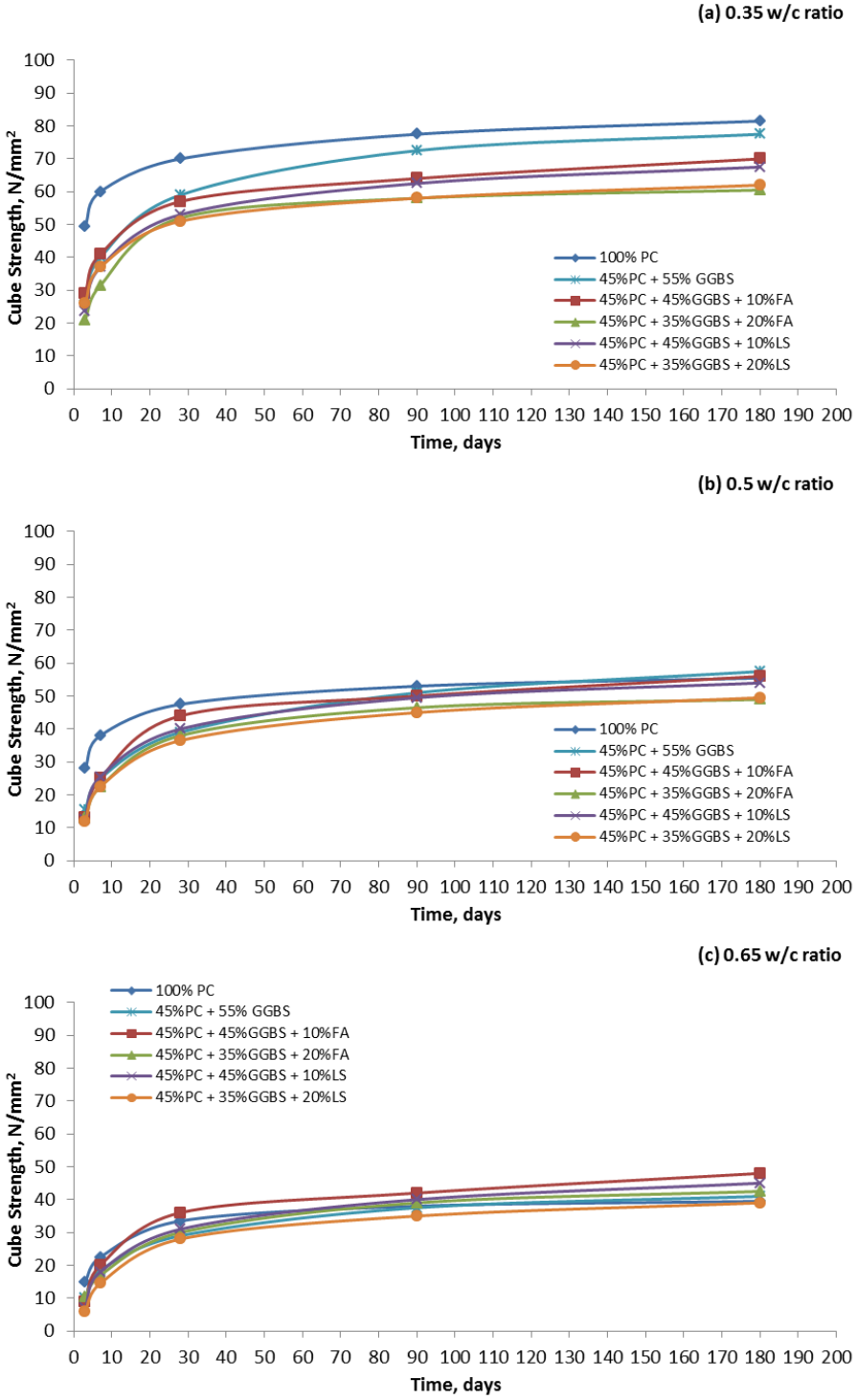


Fig 5.2: Compressive strength at 55% addition level

At 0.5 w/c ratio, the binary mix at this level was significantly lower in strength than the CEM I control mix up to 28 days. It was not until 90 days that the strength was comparable to the control mix, and at 180 days a slight increase was noted. The 10% fly ash and limestone ternary mixes gave similar results to those of the binary, and only slightly lower strength than the CEM I control mix at the later test ages. When 20% fly ash and limestone were added to the mix this had a detrimental effect on strength, giving significant reductions at all ages, compared to both the 10% ternary mixes (which were comparable to the binary) and the CEM I control mix.

At 0.65 w/c ratio, the binary mix at the earlier test ages was lower than the CEM I control. By 90 days, the strength had improved and was greater than this by 180 days. At 3 and 7 days, the ternary mixes with 10% fly ash and limestone remained lower than the CEM I control, but comparable to the binary mix. Whilst the 10% limestone ternary mix remained lower than the CEM I control mix at 28 days, the 10% fly ash ternary mix had improved with an increase in strength clearly noted. By 90 days, the 10% limestone mix had caught up with its fly ash counterpart and both had higher results than the CEM I control and binary concretes. This continued to 180 days where they gave a significant improvement in compressive strength. The 20% addition of both fly ash and limestone gave no improvement compared to 10% addition. The 28 day strengths were comparable to those of the binary concretes for 10% limestone and at 90 and 180 days they were lower. The 20% limestone was lower than the binary but better than the CEM I at this higher w/c ratio. The 20% fly ash mix remained lower than the 10% fly ash throughout testing.

5.2.3 75% GGBS Level

At all w/c ratios, the binary mixes remained lower in strength than the CEM I control at all test ages. Only at 180 days with the 0.65 w/c ratio, did the strength become comparable. The greatest difference between the two concretes was at the 0.35 w/c ratio.

The 10% ternary blends did not give improvements and indeed were significantly lower than the binary mixes at 0.35 w/c ratio. This difference was less at 0.5 w/c ratio and at the 0.65 w/c ratio the ternary blend concretes were comparable to the binary mix.

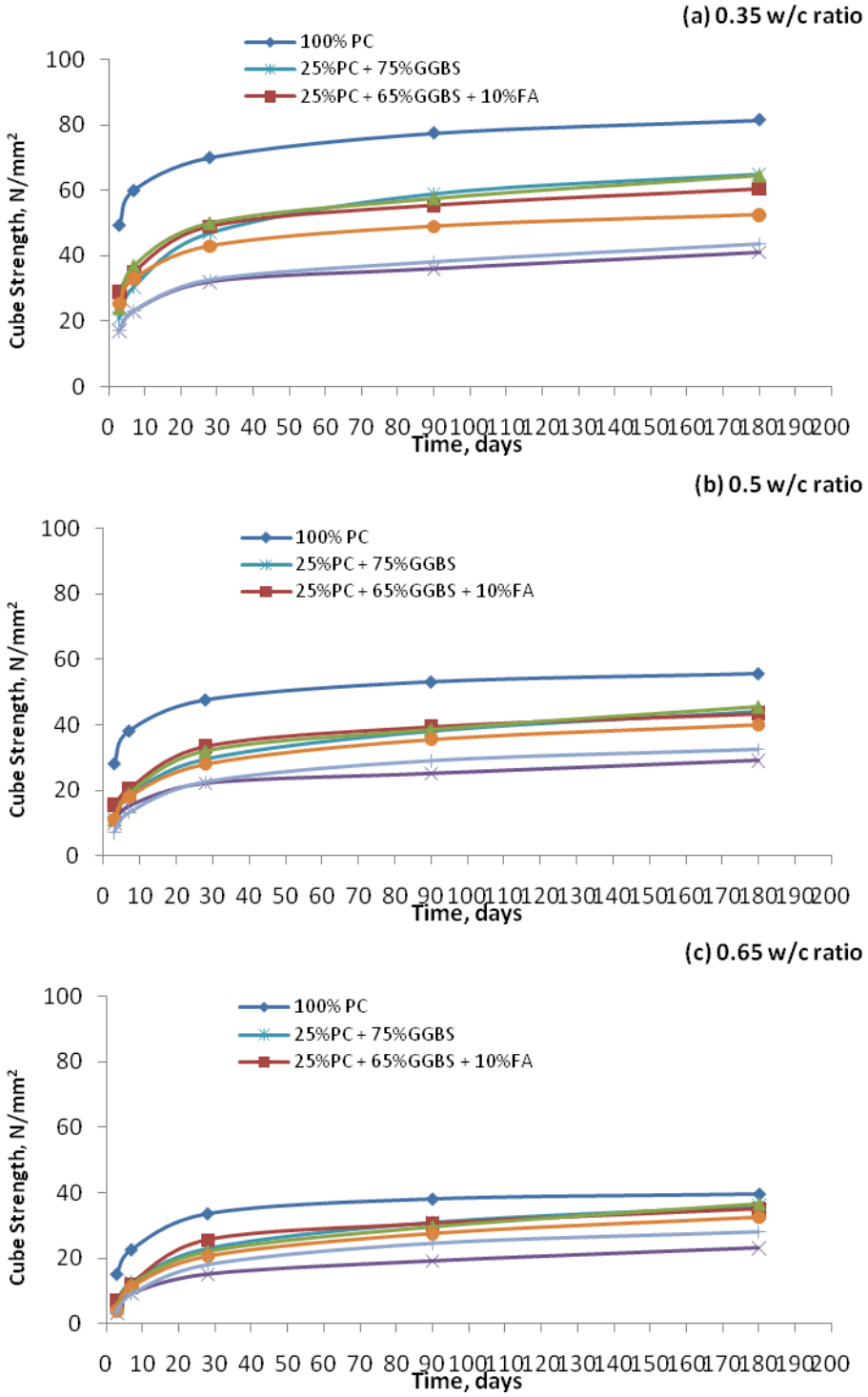


Fig 5.3: Compressive strength at 75% addition level

The 20% addition of limestone and fly ash gave no real difference, remaining significantly lower in the case of the 20% limestone blend, than the binary. The difference was less at 0.5 w/c ratio and at 0.65; the 180 day test result concrete indicates that the 20% fly ash mix was slightly greater than that of the binary concrete.

At this level, 35% limestone addition was introduced to the concrete mixes. The strength results gave a similar pattern to the other concretes, with greater reductions compared to the binary and CEM I control noted. The difference between the 20% and the 35% limestone ternary mixes was greatest at the 0.35 w/c ratio.

5.2.4 Effects of ternary materials

The effects of the GGBS binary concretes were noted, with their slower rate of early strength development and increase in long term strength clearly shown. The increase in addition level indicated a diluting effect, as the GGBS volume increased the strength decreased (*Menendez et al, 2003*). GGBS, whilst possessing cementitious properties, requires an activator to hydrate effectively (*Heikal et al, 2000*). In its simplest terms, when CEM I initially hydrates it produces alkalis and releases free lime that enables the activation of GGBS. The lower volume of CEM I, with increasing GGBS content, restricts the availability of free lime and alkalis, thus limiting the production of C-S-H and strength development (*Heikal et al, 2000*).

In the case of the fly ash ternary mixes, competition for lime is created between this and GGBS and is the likely cause for the reduction in compressive strength for the lower w/c ratio mixes. Both GGBS and fly ash require lime to enable their reaction and the formation of C-S-H (*Heikal et al, 2000*). An increase in w/c ratio increased reaction and hence the production of free lime by the CEM I resulting in reduced competition. A difference is clearer with an increase in fly ash at the higher replacement levels. The 10% fly ash ternary at the 55% level seemed of little consequence, the volume of GGBS was sufficient to reduce the effects of competition from the limited fly ash. An increase to 20% fly ash, however, inhibits strength development, as it competes for the lime with the GGBS.

It was anticipated that the addition of limestone to create ternary mixes would improve the initial strength development of GGBS as suggested by Menendez et al (2003), providing a greater quantity of limestone to assist in the reaction of GGBS. However, at the lower replacement level, the addition of 10% limestone was of no positive benefit when compared to the binary. In fact, it had the negative effect of reducing strength, making the mix comparable with its 10% fly ash counterpart. This contradicted the study of Menendez et al (*2003*) who showed that a mix consisting of 55% CEM I + 35% GGBS + 10% limestone had a higher compressive strength, than a CEM I control at 3 and 7 days for a mix with a w/c ratio of 0.5. Menendez et al (*2003*) attributed the increase to the acceleration of hydration at an early age. Whilst it does not have pozzolanic properties, or produce C-S-H, limestone acts as nucleation sites of calcium hydroxide during early hydration accelerating the hydration of C_3S (*Pera et al, 1999*). The strength of their mix was shown to be considerably improved compared to the binary mix, making it comparable, if not slightly improved compared to the CEM I.

Whilst this effect was not seen at the lower replacement level, it may be accountable for the increase in strength at the 55% level, more clearly seen with an increase in w/c ratio to 0.65, indicating that the reaction of limestone is dependent on the volume of water available for hydration (*Menendez et al, 2003*). The 10% limestone ternary mix at this level is comparable with the binary, and shows a slight improvement at early ages. This is further supported by Mun et al (*2007*), although their study was carried out on mortar. They suggest the improvement, in this instance, is due to limestone reducing the film formation on the surface of the GGBS particles by producing alkali during early hydration, thus destroying an acid film formed during initial hydration (*Detweiler et al, 1996*) and promoting hydration products. The limestone substitutes sulfate for ettringite promoting the hydration of GGBS (*Singh & Garg, 1995*).

It is unclear why there are contradictions between Menendez et al's findings and those reported in this study. It may be due to differences in the properties of materials used. Tsivilis et al (*1999*) suggested that the influence of limestone depends on the C_3A content of the clinker. In Chapter 3, the reported properties of the CEM I used in this study showed a C_3A

value of 5.8%, much higher than the 2% reported by Menendez et al. Vuk et al (*2001*) also suggest that the C_3S content can also affect the limestone. The CEM I used in this study reported higher C_3S than that of Menendez et al, 65.6% and 58% respectively. The fineness may also be of importance (*Pera et al, 1999*) as the finer materials can aid the packing and formation of a denser structure, improving the strength of concrete.

5.4 Cement Additions Efficiency Factor

Past studies have used compressive strength data to determine cementing efficiency. As early as 1967, Smith discussed the effect of fly ash and assumed it to have a cementing efficiency, in which a weight of fly ash would be equivalent to a weight of cement, thus determining an effective water cement ratio using the following formula:

$$w/c_s = \frac{w}{C+KF} = \frac{w}{c}\left[\frac{1}{1+(KF/C)}\right]$$

[Eq 5.1]

Where:

W	=	weight of free water
C	=	weight of cement
F	=	weight of fly ash
w/c_s	=	effective water cement ratio of a concrete with regard to its strength
K	=	cementing efficiency of an fly ash relative to cement

Smith used a value of 0.25 for *K* (*Smith, 1967*). Wong & Razak (*2005*) refer to Smith's work and assumed *K* to be unique for each type of fly ash used in the study. But whilst 0.25 was suitable for Smith's study, a constant K factor does not exist, Papadakis & Tsimas (*2002*) found that the *K* value for fly ash with low calcium to be 0.5 at 28 days.

Babu & Rama Kumar (*2000*) studied the efficiency of GGBS by using a variation on the 28 day strength to w/c ratio relationship. Smith's formula was adapted for GGBS by replacing *F* with *G* for GGBS. Babu & Rama Kumar calculated that at 28 days the overall strength efficiency factor varied from 1.29 to 0.7 for the range of GGBS levels from 10% to 80%.

Whilst these papers followed similar formulae, Byars' study in 1995 used a simpler determination of the binder cementing efficiency. By using the following formula, a binder cementing efficiency was calculated based on the content of cement additions.

$$Kc = \frac{fc(t)}{c}$$

[Eq 5.2]

Where:

Kc	=	*cementing efficiency*
fc(t)	=	*strength at a specific age*
c	=	*cement content*

All of these previous studies refer to binary mixes and to date no studies have reported the efficiency of ternary blends. Whilst a binary mix can be related, or compared directly to its corresponding CEM I, a ternary mix needs to be examined to assess the effects of the third cementing addition compared to a binary mix. With this is mind Byars' equation can be adapted to find the relative binder efficiency for ternary mixes.

$$R_{cem} = \frac{Kc_b}{Kc_{cem}} \qquad R_{bin} = \frac{Kc_t}{Kc_b}$$

[Eq 5.3]

Where:

R_{cem}	=	efficiency relative to CEM I
R_{bin}	=	efficiency relative to the binary mix of a specific addition level
Kc_{cem}	=	cementing efficiency of CEM I
Kc_b	=	cementing efficiency of binary mix
Kc_t	=	Cementing efficiency of ternary mix

To this end, the cementing efficiency has been calculated for both binary mixes relative to CEM I and ternary mixes relative to binary mixes at the specific level, and w/c ratio, and is shown in Figures 5.4 to 5.7.

5.4.1 Binary Cementing Efficiency

By examining the calculated cementing efficiency, the effects of the additional materials become more apparent. It is seen from the binary mixes in Figure 5.4 that at the lower w/c ratio, beyond 28 days the 35% level had become more efficient in strength gain than 55% and 75% levels. An increase to 0.5 w/c ratio shows, that whilst the 35% level is still efficient beyond 28 days, it is not as obvious and the lower volume of materials to water has improved the 55% replacement level making it more comparable for the longer-term, 180 days. Babu & Kumar (*2000*) reviewed a number of earlier studies and found that for a concrete with 30% of GGBS, the average efficiency at 28 days was 1.02 across a range of w/c ratios from 0.26 to 0.55. Whilst this study had a wider range of w/c ratios (0.35 to 0.65), the relative cementing efficiency of the 35% replacement level was similar to that reported by Babu & Kumar.

An increase in w/c ratio has a very clear effect on the cementing efficiency at early ages. This improved markedly at the 55% level and it appears that the increase in w/c ratio aided the hydration of the CEM I, to produce $Ca(OH)_2$ and activate the GGBS. The rate of pozzolanic reaction clearly depends on the availability of water and lime; this is further indicated at the 75% replacement level, which does not match the development of strength for the other mixes. The diluting effect of the binary materials means that there is insufficient lime being produced by the limited volume of CEM I, available for reaction. The high w/c ratio did finally indicate comparable results by 180 days for this mix, compared to the CEM I.

Wong & Razak (*2005*) state that the reaction of GGBS gives no immediate or obvious strength enhancement. They also state that the loss in strength is proportional to the GGBS level, also reflecting a dilution effect and the slow rate of pozzolanic reaction. In addition, Wong & Razak (*2005*) claimed that the w/c ratio did not affect efficiency, but it is clear from this study that there was an effect. However, Wong & Razak's study covered a limited range of 0.27 to 0.33 w/c ratio. It is therefore clear that greater increases in w/c ratio affects the cementing efficiency of the mix combinations.

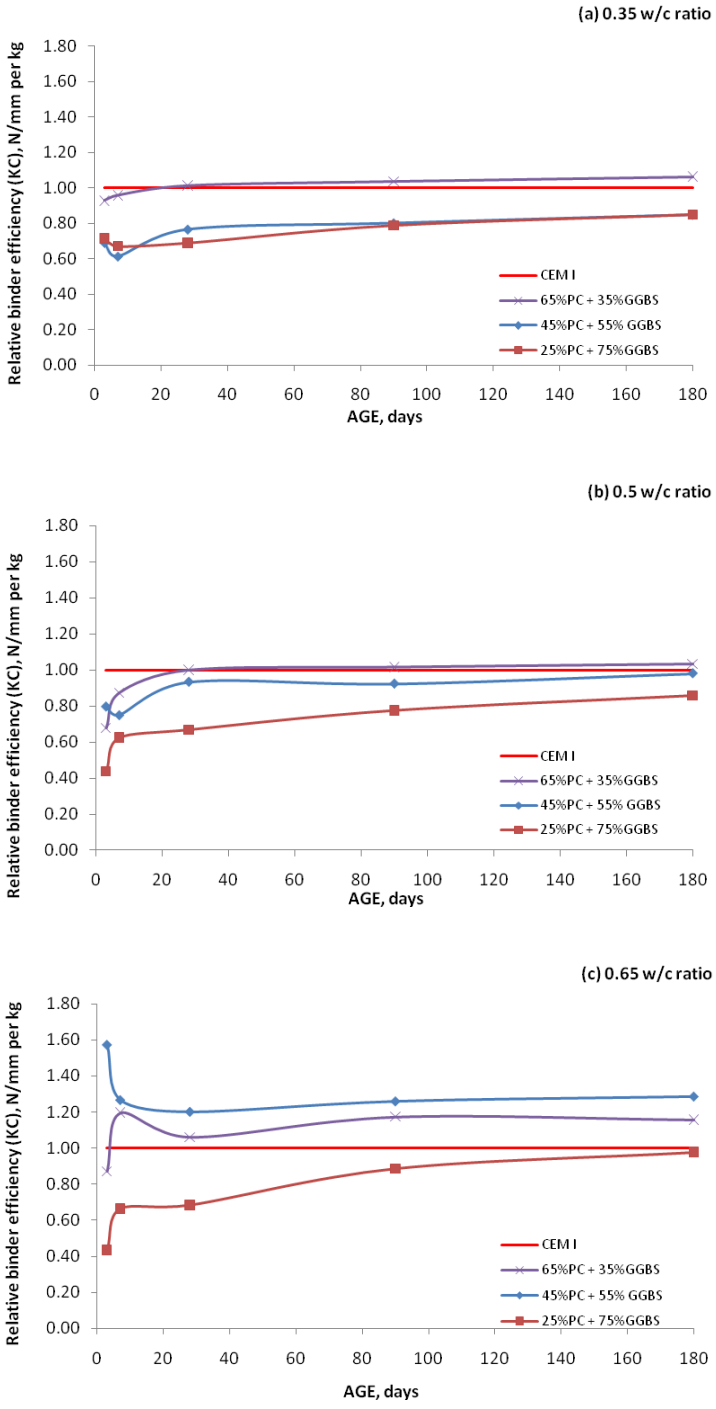


Fig 5.4: Binder cementing efficiency for binary levels relative to CEM I

5.4.2 Ternary Cementing Efficiency

Earlier studies have previously shown cementing efficiencies for binary mixes and these have been discussed in the context of this study already. It is here that the ternary mixes will be compared to the binary mixes, as shown in Figures 5.5 to 5.7, to examine the effect of these additional materials.

At the lower 35% level for the 0.35 w/c ratio, it is clear that the effect of both fly ash and limestone additions was negative. In general, this was also the case for the 0.5 w/c ratio. However, the 10% fly ash mix did have an initial effect of increasing cementing efficiency at 3 days. This efficiency increased with w/c ratio and was maintained throughout the 180 day testing. As discussed earlier, the fly ash is likely to compete with GGBS for lime, and an increase in w/c ratio causes a higher rate of initial hydration, acting as a nucleation site, of the CEM I, producing sufficient lime $Ca(OH)_2$ for both additions (*Menendez et al, 2003*). With regard to the limestone ternary, it is more likely that, given its ability to fill pore spaces, creating a denser microstructure, this is the cause of the initial strength, together with the provision of additional lime for reaction with the GGBS.

An increase to the 55% level indicated improvements in cementing efficiency at earlier ages for the majority of mixes. The reaction of fly ash at the earlier ages, combined with that of GGBS, had increased cementing efficiency, but with an increase in time, the competition for lime increased, as less was being produced by the hydrating CEM I, and the cementing efficiency decreased, yet remained higher than the binary, or at least comparable, across the range of w/c ratios. The increase in 20% fly ash increases competition thus reducing the cementing efficiency. The limestone addition followed a similar trend to the fly ash ternary mixes. Figure 5.7 shows that an increase in replacement level to 75% reduces the cementing efficiency for the lower 0.35 w/c ratio. The fly ash ternary mixes were comparable at early ages, and the 20% fly ash remained comparable through to 180 days. With an increase in w/c ratio, the early cementing efficiencies were clearly improved up to 28 days for the 10% and 20% fly ash more significantly for the former at 3 days. This may be due to two factors. The first being that competition for lime, with the GGBS, may not occur initially as there is sufficient lime being produced by the hydrating CEM I, hence the sudden drop in cementing efficiency at 7 days,

when hydration of the CEM I begins to slow and therefore the production of lime is reduced. Secondly, it may also be due to a filler effect similar to that of the limestone, where it is filling pores within the structure to create a denser microstructure improving strength at this early age.

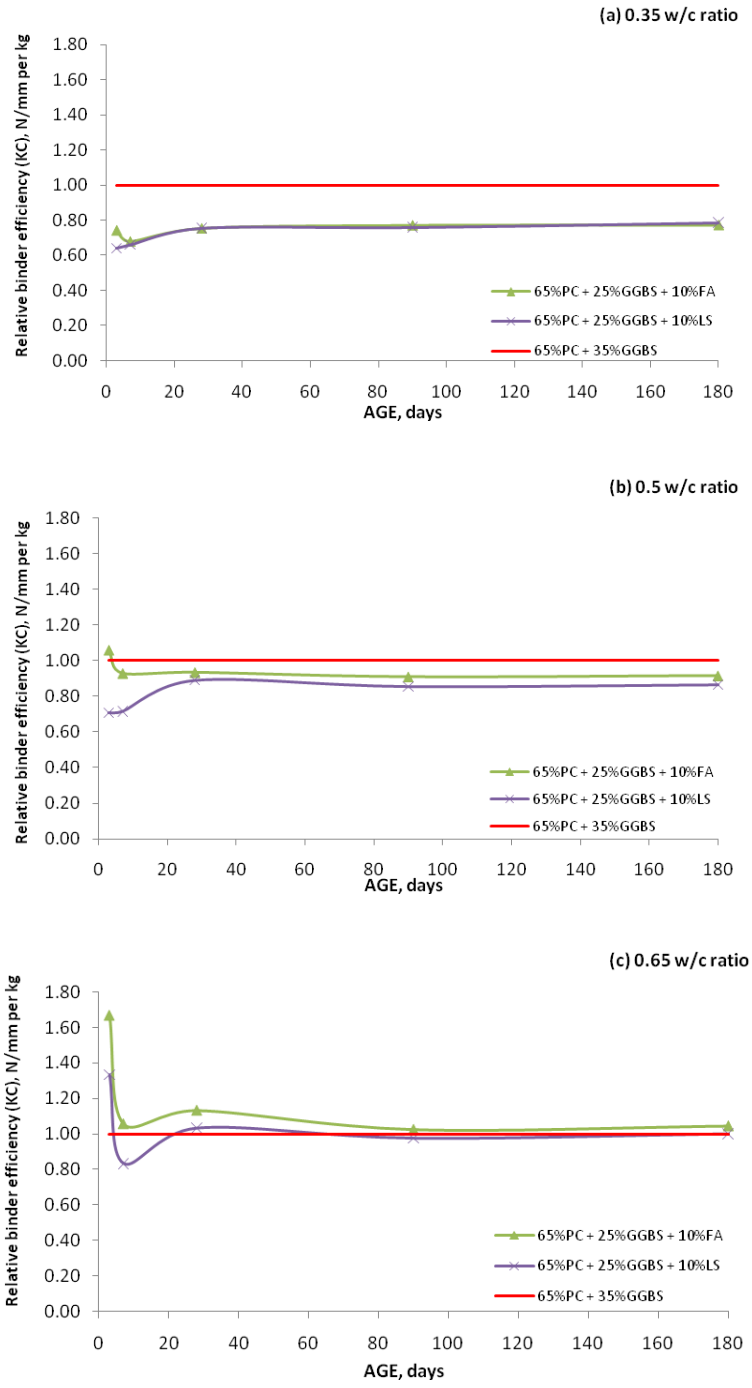


Fig 5.5: Binder cementing efficiency at 35% addition level relative to binary mix

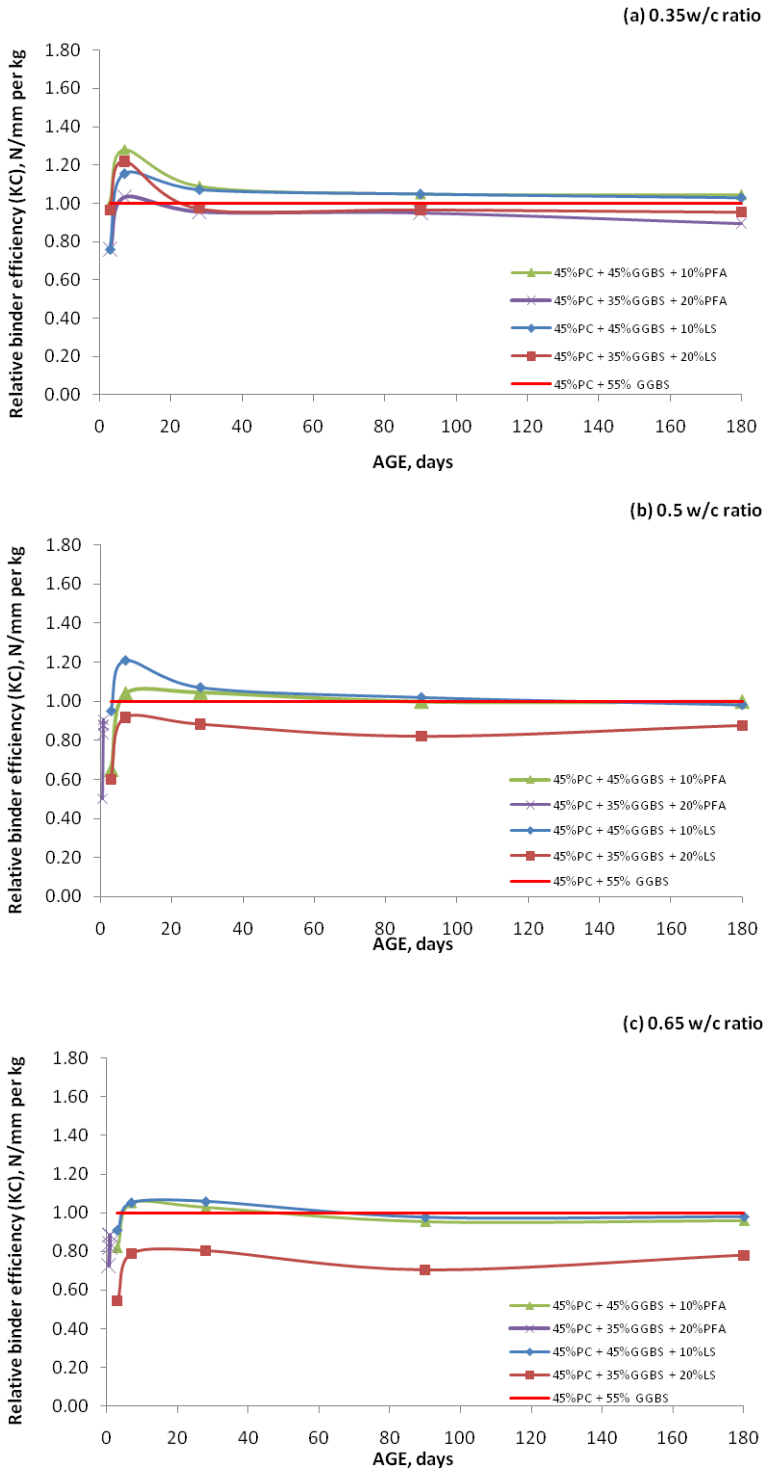


Fig 5.6: Binder cementing efficiency at 55% addition level relative to binary mix

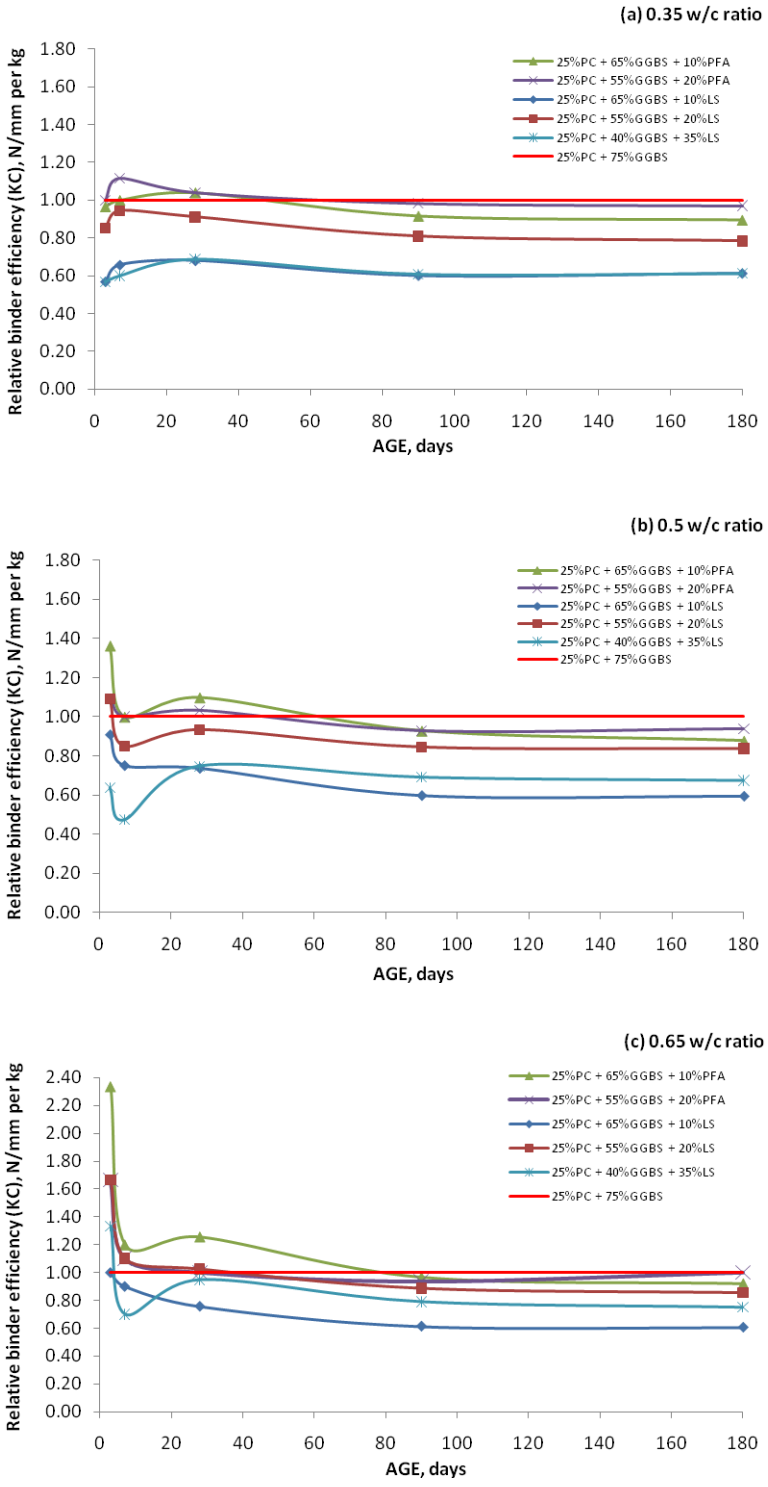


Fig 5.7: Binder cementing efficiency at 75% addition level relative to binary mix

5.5 Equivalent Strength of 40 N/mm^2

It evident from the results of the binder cementing efficiency that in order for binary or ternary mixes to reach an equivalent strength at 28 days to that of CEM I, the w/c ratio requires modification, in accordance with the content and type of additions used for each mix combination. Papadakis & Tsimas (*2002*) use the *k-value* to calculate the possible w/c ratio for binary mixes, as did Smith (*1967*) and then Wong & Razak (*2005*) subsequently. Given that test results provide data for each mix at 28 days, it is possible to interpolate to an equivalent strength of 40N/mm^2 at 28 days by plotting the strength data for each addition level, to give a required w/c ratio as shown in Table 5.1. This equivalent strength was chosen, as it is the specified minimum strength class limit for the majority of exposure classes in BS 85000-1. The w/c ratio can be assumed to be the point at which the 40N/mm^2 strength intersects the reported data for 28 days plotted across the range of w/c ratios as shown in Figure 5.8.

Table 5.1: Water cement ratio for equivalent strength of 40N/mm^2 at 28 days

Combination	Water cement ratio
100% PC	0.57
65%PC + 35%GGBS	0.41
65%PC + 25%GGBS + 10%FA	0.53
65%PC + 25%GGBS + 10%LS	0.5
45%PC + 55% GGBS	0.49
45%PC + 45%GGBS + 10%FA	0.56
45%PC + 35%GGBS + 20%FA	0.47
45%PC + 45%GGBS + 10%LS	0.5
45%PC + 35%GGBS + 20%LS	0.46
25%PC + 75%GGBS	0.44
25%PC + 65%GGBS + 10%FA	0.43
25%PC + 55%GGBS + 20%FA	0.42
25%PC + 65%GGBS + 10%LS	0.25
25%PC + 55%GGBS + 20%LS	0.38
25%PC + 40%GGBS + 35%LS	0.28

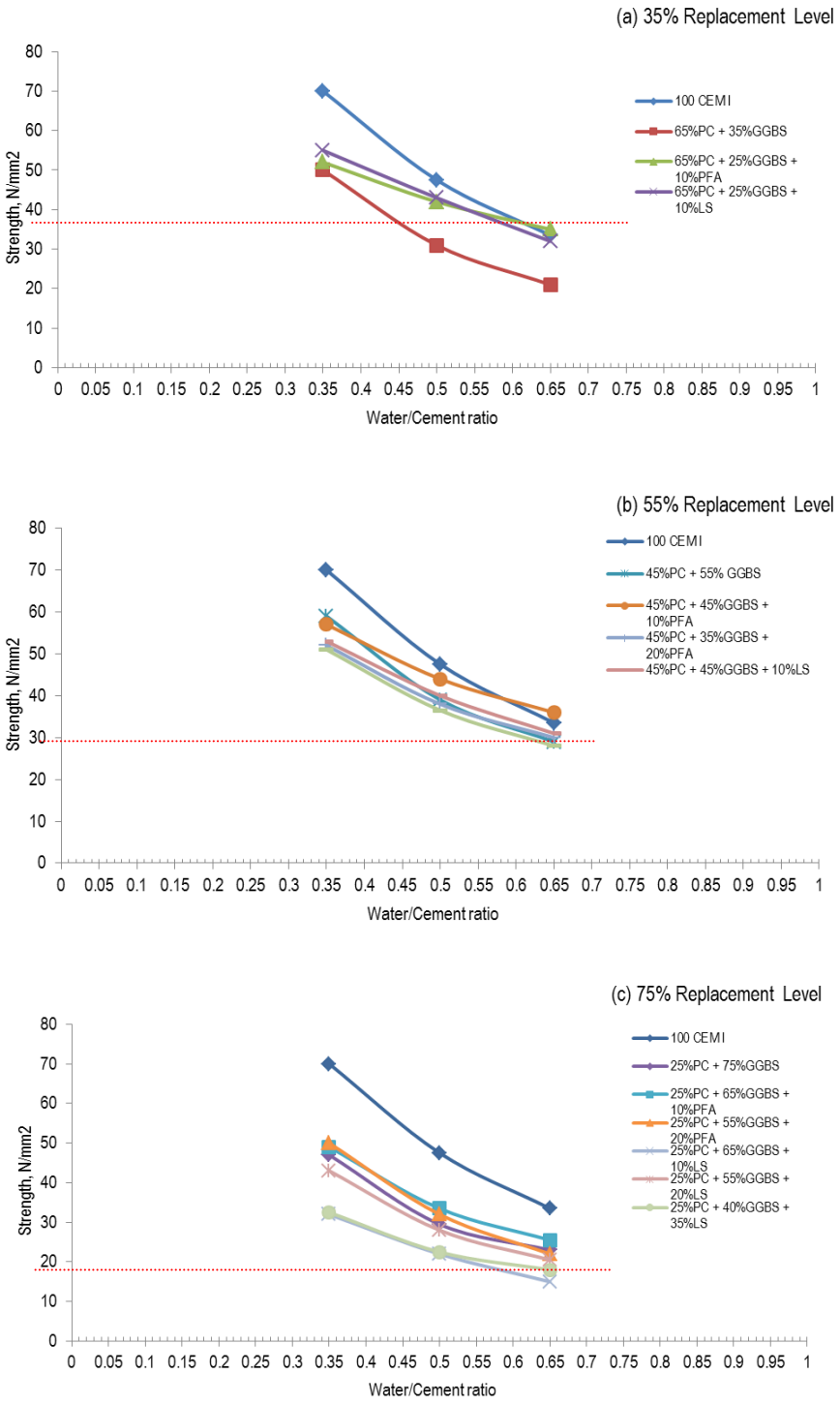


Fig 5.8: Equivalent strength of 40N/mm² at 28 days

It was determined that the CEM I required a w/c ratio of 0.58 in order to achieve a strength of 40 N/mm^2 at 28 days. By adding 35% GGBS, the required w/c ratio reduced to 0.43 but rose at 55% level to 0.48 before reducing again at the 75% level to 0.41. The reduction in w/c ratio with the addition of GGBS was reasonable; however, it might have been expected to reduce w/c ratio as the GGBS level increased. It is unclear how the slight increase at the 55% level occurred, although it still remains lower than the CEM I. This may be due to the gradient of the plotted curve and therefore not truly indicative of the equivalent strength. There is a difference in strength from 0.35 to 0.5 w/c ratio and it has already been discussed that an increase in w/c ratio to 0.5 improved the 55% level significantly, compared to that at 0.35 w/c ratio.

The addition of ternary materials at the 35% level indicated that a w/c ratio of 0.5 would be required to achieve an equivalent strength of 40 N/mm^2. A lower w/c ratio would give a higher strength at this level of addition. At the 55% level, the 10% additions again showed an increased water demand, whilst the 20% additions indicated a reduction in water demand to less than the binary. For the 75% level, the inclusion of fly ash as a ternary material had the effect of increasing the w/c ratio slightly. The 10% and 35% limestone additions did not give results due to the low recorded strengths across the range of w/c ratios, whilst the 20% limestone provided a lower water demand from those recorded. This is likely to be due to the reported results plotted to give a lower gradient of curve as shown in Figure 5.8 (c).

Fly ash, as a binary material when used with CEM I, is reported to reduce the water demand, in turn allowing a lower w/c ratio, attributed to by the spherical shape of the fly ash particles (*Stuart et al, 1980*), but when used as a 10% ternary addition the water demand is slightly increased at the 35% and 55% levels. The pozzolanic activity of the fly ash is minimal with the 10% addition. However, a 20% fly addition at the 55% level did indicate an improved strength gain with a lower w/c ratio required to reach an equivalent strength of 40N/mm^2. Using a lower w/c ratio can result in some offset against strength reduction. In order to match strength at 28 days with a lower w/c ratio 20% fly ash would be recommended for both the 35% and 55% levels. This is also true of the limestone addition. The limestone generally acts as a filler between the CEM I and GGBS particles, reducing the space available for water. These

estimations indicate simply the changes to w/c ratio that may be required in order to match strength and are influenced by reactivity of the materials and packing. In all cases the water would be fixed at 165ml/m^3 and it would mean adjusted the volume of materials to meet the required w/c ratio.

5.6 Strength and Packing Density

The development of compressive strength is due to the chemical reaction between cement and water creating bonds between the materials. This hydration process leads to products forming including C-S-H that fills voids within concrete. The voids vary and may be caused by spaces that remain after excess water has been removed, and whilst hydration products fill many of these voids, some remain and are detrimental to the strength of the concrete. Neville stated that a lower number of voids provide a denser concrete with greater strength (*Neville, 1995*). However, on review of the data, this did not necessarily follow. Whilst the combination of additions reduced the voids ratio overall, not in all cases did the strength improve.

It was expected that all GGBS levels would increase the w/c ratio to achieve 40 N/mm^2 and would result in an increase in voids ratio. The voids ratio, itself, corresponds to the solid material before any effects of water (hydration or reaction) have taken place and is based on the theoretical model proposed by De Larrard discussed in Chapter 3 (3.7.2). The excess water fills spaces where C-S-H bonds have not formed, increasing the void ratio and decreasing the strength of concrete. The volume of solid material reduces with the increase in w/c ratio and therefore the packing density may reduce. The use of a vibration plate during the casting process reduces the formation of voids from entrapped air but there still remains opportunity for voids to be present if this has not been done effectively, indeed not all air will be removed effectively. Due to the varying fineness of the materials also, as the volume of GGBS and ternary additions increased, the voids ratio decreased.

For the 35% addition level, shown in Figure 5.9, as with the other levels, the reduction in voids ratio with the addition of finer material, compared to the CEM I, is clear. The lower

voids ratio and comparable strength was seen for the binary mix at 28 days, across the range of w/c ratios, but with the addition of ternary at the lower w/c ratio, despite a reduction in voids ratio, there was no improvement in strength. An increase to 0.5 w/c ratio did give more comparable results for both ternary mixes but they did remain more than the binary and CEM I. At the 0.65 w/c ratio, an increasing voids ratio had the effect of increasing strength of both ternary mixes, improving it compared to the binary mix. The void ratio is dependent on the packing of the solids within the matrix and not the formation of the concrete microstructure itself. However, the reactivity of the materials is important in relation to the developing structure, as a result of the reaction of GGBS more C-S-H is produced to fill the pore spaces reducing voids within the concrete and in turn creating a stronger matrix.

By 180 days, (Figure 5.9) the strength has increased due to greater reactivity over the longer term, but the same trend occurred, as at 28 days for the 0.35 w/c ratio. An improvement is seen at 0.5 w/c ratio, with the binary mix increasing strength compared to CEM I, whilst the ternary mixes both remained slightly lower. As previously discussed, an increase in w/c ratio to 0.65 indicated the better improvement at this replacement level allbeit still a lower strength than the mixes at the other two w/c ratios, it is still higher than the CEM I.

As already discussed, an increase in the GGBS level affects the compressive strength and this depends on the w/c ratio. At 28 days with 55% replacement the voids ratio is lower for both the binary and the ternary mixes but no improvement was seen compared to the CEM I mix at the lower 0.35 w/c ratio, although they are comparable with each other. As seen with the 35% level, an increase to 0.5 w/c ratio showed little improvement again and a further increase to 0.65 w/c ratio makes all mixes more comparable, in terms of the strength, with the CEM I with the exception of the 10% fly ash ternary that was slightly improved. This ternary mix was clearly the better at this test age across the range of w/c ratios and yet by 180 days the behaviour changed.

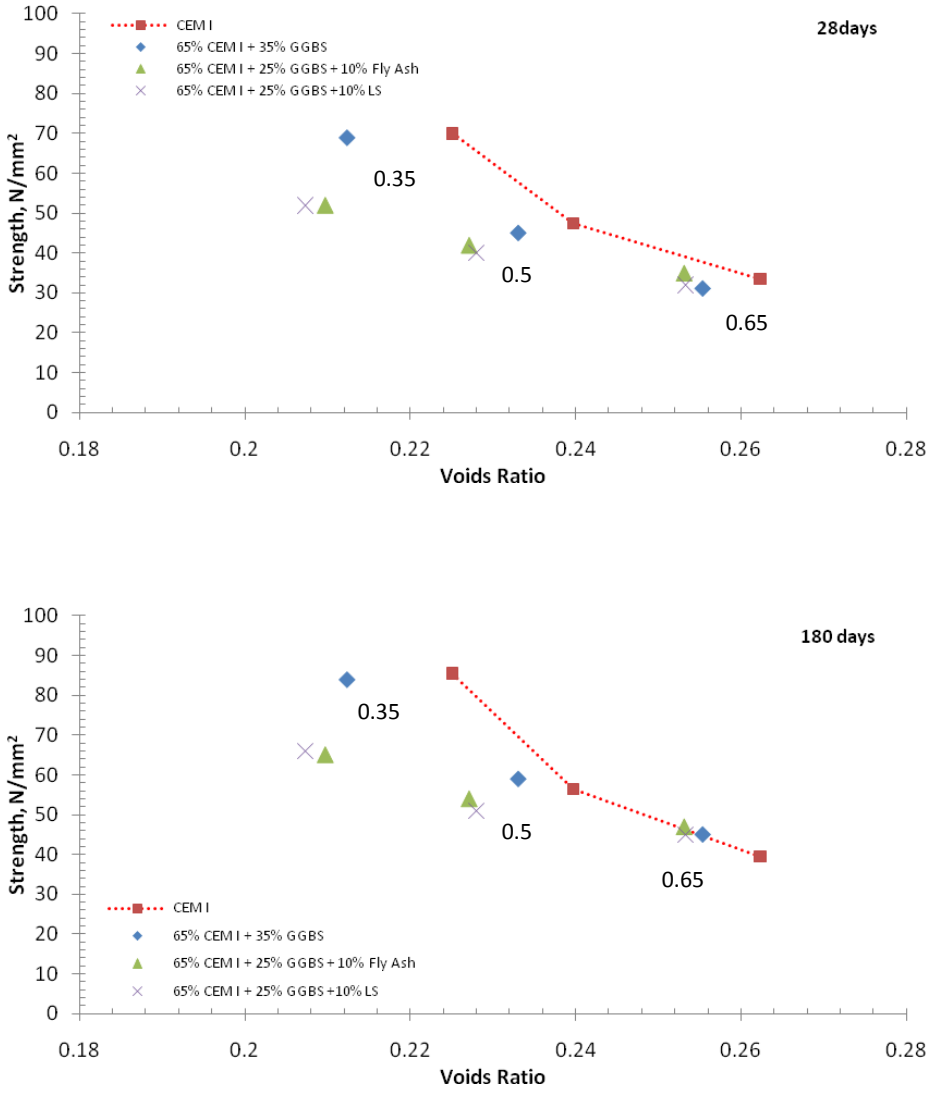


Fig 5.9: Strength and void ratio of 35% addition level mixes

At 0.35 w/c ratio, the binary and ternary mixes were consistently lower than the CEM I despite their lower voids ratio. An increase to 0.5 w/c ratio at 180 days showed the binary and both 10% ternary mixes to be comparable if not slightly improved with regards to the strength of CEM I. The increase to 0.65 w/c ratio had the effect of improving the 10% ternary mixes beyond both the binary and the CEM I concretes, with the 10% limestone slightly higher than the fly ash. The 20% additions did little to improve the long-term strength of the concrete. The longer curing time allowed for further reactivity of the cement paste,with the hydration products filling some of the cement and water-filled space. Capillary voids are created and in high w/c ratio concrete these can be a large as 3 to 5µm, thus affecting the overall strength of concrete adversely. For lower 0.35 w/c ratio, the capillary voids range from 10 to 50nm (*Mehta & Monteiro, 2006*).

An increase in addition level to 75%, whilst reducing the voids ratio slightly, gave no improvement in compressive strength at all w/c ratios at 28 days, as the strength depends on the reactivity of the powder. The longer curing period to 180 days also gave poor results for the combination mixes. At 0.65 w/c ratio, the compressive strengh increased with the 20% fly ash comparable with the CEM I in this instance, as shown in Figure 5.11. It is likely that the fly ash and the GGBS are both competing for the limited amount of $Ca(OH)_2$ being produced by the CEM I, given its reduced volume, the increase in w/c ratio may be aiding the reaction of the combined materials, yet it is widely established that both materials reduce water requirements to produce a standard consistency as discussed previously, in Chapter 4.

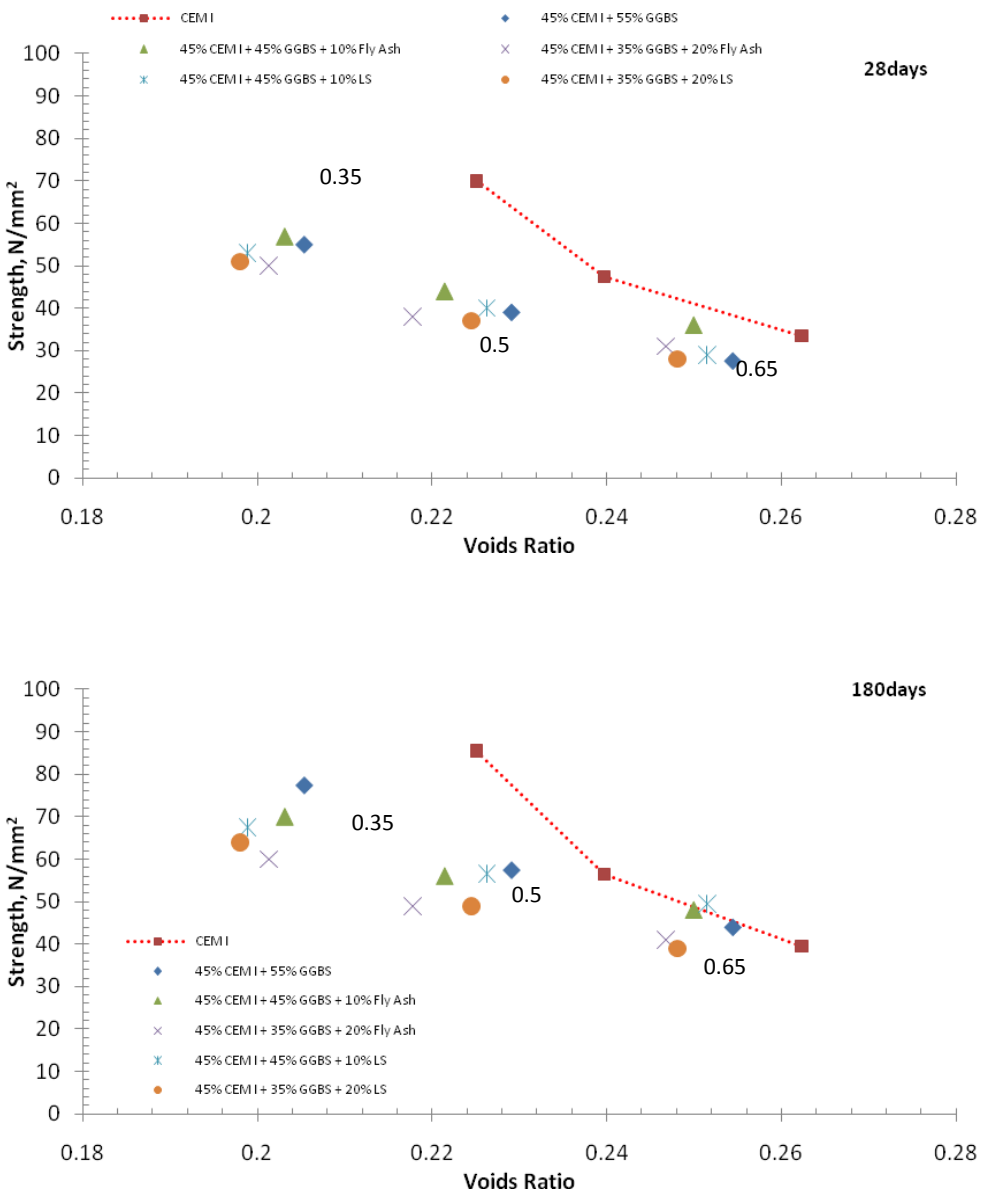


Fig 5.10: Strength and void ratio of 55% addition level mixes

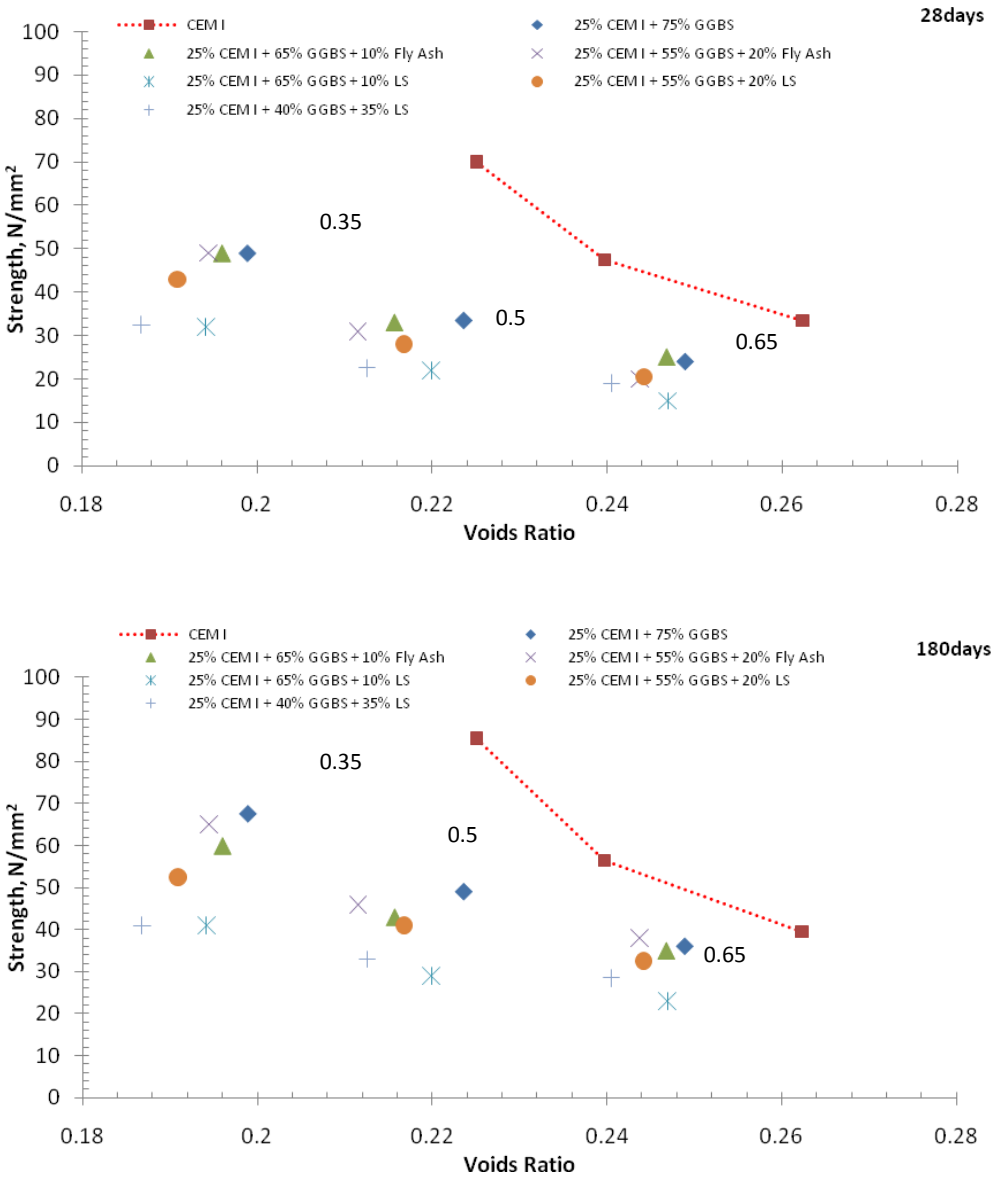


Fig 5.11: Strength and void ratio of 75% additions level mixes

5.7 Relationship Between Concrete and the Cement Paste Matrix

5.7.1 Compressive Strength

Selected cement pastes samples were cast and tested for compressive strength in order to ascertain the existence of any correlation between them and their concrete counterparts. The significant difference between the concrete and the cement paste would be the addition of aggregates creating an interfacial transition zone between them and the cement paste within the concrete structure. This being the only significant difference one may expect some correlation and indeed, that does seem to be the case on face value, when examining the samples collectively as shown in Figure 5.12.

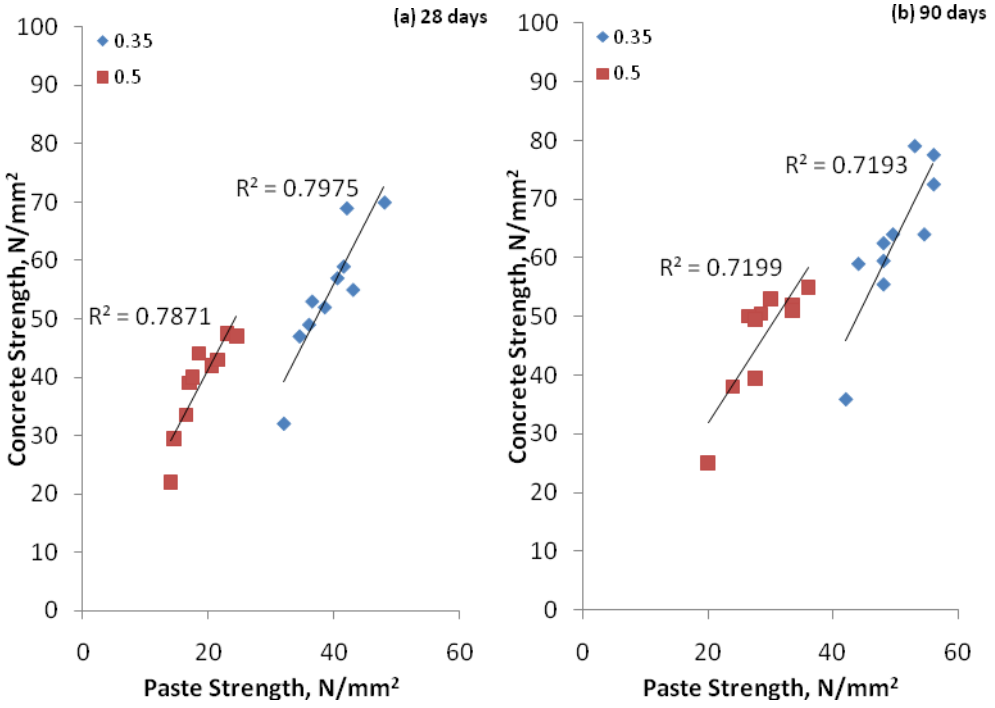


Fig 5.12: Comparison of compressive strength of paste and concrete sample

In general it would appear that the compressive strength of concrete increased with that of the cement paste samples tested for both w/c ratios and test ages. However, when viewed independently in Figure 5.13, it is observed that the rate of increase is dependent on the cement addition and level of replacement. Whilst the trends are similar no assumption can

be made, furthermore, no mathematical model was developed in order to predict the compressive strength of concrete from that of its cement paste counterpart.

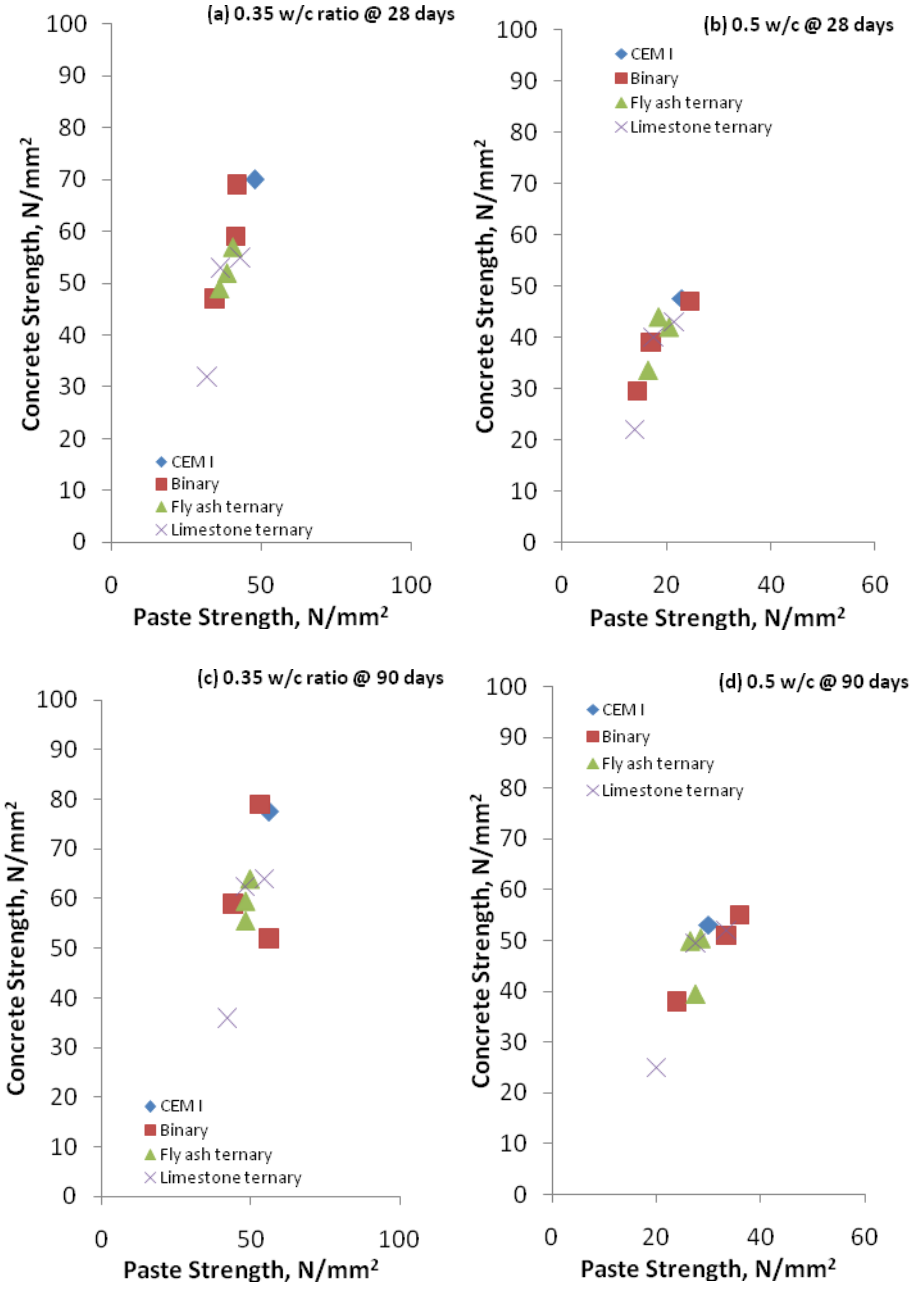


Fig 5.13: Compressive strength of concrete against paste samples

5.7.2 Strength-Porosity Relationship

There are a number of factors influencing the compressive strength of concrete, in addition to the more obvious loading parameters one must also take into consideration the internal structure of the concrete including the cement paste matrix and the interfacial transition zone. Figure 5.14 summarises the influential variables affecting the strength of concrete. It is clear that porosity is a notable factor affecting the strength of concrete. Kumar & Bhattacharjee (*2003*) discuss the well-established Abrams rule that both strength and porosity depend upon w/c ratio as per the following expression:

$$fc = \frac{k_1}{k_1^{w/c}}$$

[Eq 5.4]

Where *w/c* is the w/c ratio and k_1 and k_2 are empirical constants.

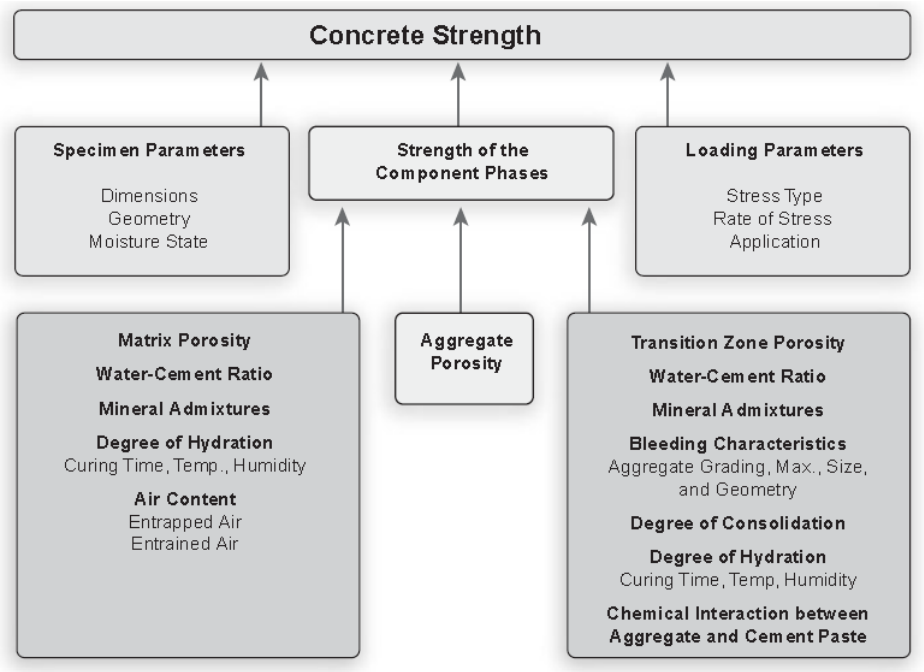


Fig 5.14: Influential factors of concrete strength (Mehta & Monteiro, 2004)

Kearsley & Wainwright discuss a number of variations on Abram's basic principle, many of which take into consideration the sir content and degree of hydration (*Kearsley & Wainwright, 2002*). However, Kumar & Bhattacharjee argue that indirect relationships such as pores present within the hardened concrete matrix due to poorly compacted materials, the changing pore system with degree of hydration and chemical changes are generally overlooked (*Kumar & Bhatacharjee, 2003*). As Neville & Brooks state, most expressions assume that the fresh cement is fully compacted thus containing no accidental or entrapped air. They further state that porosity's corresponding relationship with strength is independent of whether the capillary pores within the concrete strength, are full of water or empty. This would depend on the w/c ratio of the mix design or indeed whether any additional water ingresses during hydration (*Neville & Brooks, 2007*). With regards to concrete samples used in this study the mixing process involved the use of a vibration table to mitigate any effects from inadequate compaction, all samples were cured in a curing tank for durations of 3, 7, 28, 90 and 180 days undergoing the same preparations for each test performed to limit variables.

As previously discussed one of the obvious differences between cement paste and concrete is the aggregate that creates the ITZ. Whilst the porosity of the cement matrix during hydration is key, a diagrammatic representation based on the proportions by volume of the constituent materials before and during hydration as per Neville & Brooks (2007) is shown in Figure 5.15, the w/ ratio governs the porosity of the ITZ hence its relationship with strength. It is therefore postulated by many that there is an inverse relationship between porosity and the compressive strength of concrete (*Kearsley & Wainwirght, 2002; Kumar & Bhattacharjee, 2003; Mehta & Monteiro, 2007*). This relationship is expressed by the following equation:

$$S = S_o e^{-kp}$$

[Eq 5.5]

Where S is the strength of the material which has a given porosity p

S_o is the intrinsic strength at zero porosity

K is constant

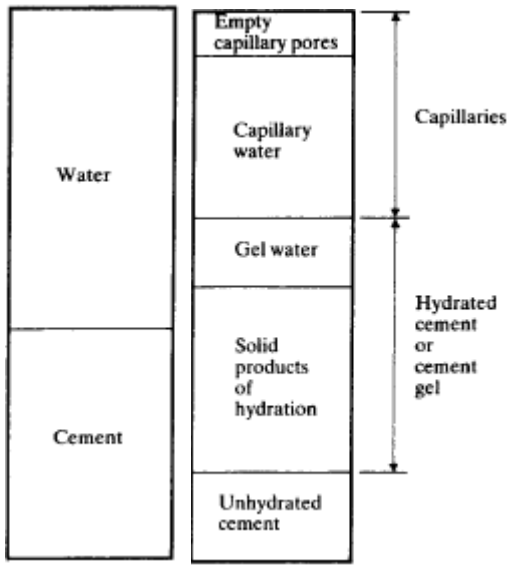


Fig 5.15: Diagrammatic representation of the volumetric proportions of the composite materials before hydration (a) and during hydration (b)

Naturally the porosity of concrete is likely to affect other properties with regards to durability and permeation and these will be discussed in subsequent chapters. The porosity was determined by Mercury Intrusion Porosimetry (MIP) on selected paste samples at 28 and 90 days. Both the critical pore size and the total effective porosity were determined using this method but Kumar & Bhattacharjee state that there are a number of factors that need to be taken into consideration. The extent of the porosity depends on the nature of the pores, the size of the smallest pores likely to be present and also the maximum intrusion pressure applied. Whilst this may be apparent it may well mean that gel pores and indeed, closed pores, can remain non-intruded (*Kumar & Bhattacharjee, 2003*). The MIP also disregards the true size of the pore measuring only its entry size, referred to by Diamond as the "ink bottle" effect (*Diamond, 2000*).

Figure 5.16 shows the compressive strength against porosity for the 35% replacement level compared to the CEM I control mix for both the lower and mid-range w/c ratios. It is evident that for each mix combination, as porosity decreased strength increased over time, thus concurring with the authors previous discussed. As the w/c ratio increased from 0.35 (a) to 0.5 (b) the porosity is greater and the strength is lower, as would be expected with the excess

water often being trapped within the concrete matrix forming capillary pores over time. The higher porosity, measured at 3 days, decreases as the hydration product are formed, the larger capillary pores become filled with, what Mehta & Monteiro describe as, (microporous?) hydration products that are characterised by a finer pore network (*Mehta & Monteiro, 2007*).

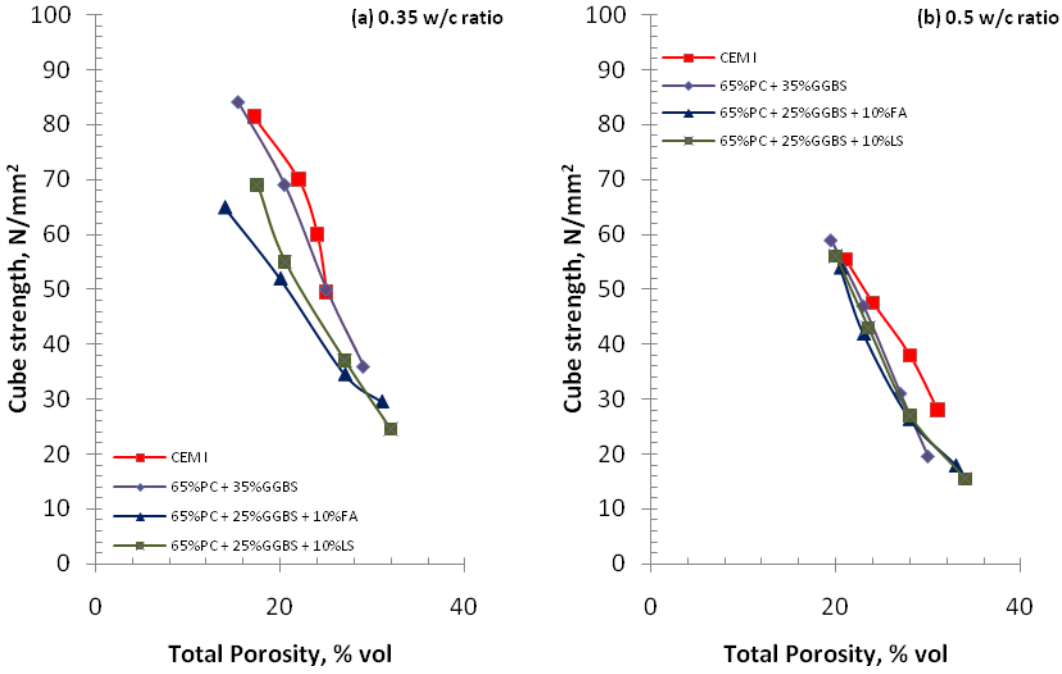


Fig 5.16: Cube strength aginast total porosity at the 35% replacement level

The effects of the additional materials is seen at the 35% replacement level as the binary mix shows both lower porosity and increased strength than the CEM I control mix by 90 days for both w/c ratios. The effect of both ternary additions is clearer for the lower w/c ratio. Whilst they have improved porosity the strength, though increasing with age, cannot compete with that of the binary mix. The increase in w/c ratio gave far more comparable results by 90 days clearly indicative of the effects of additional water within the capillary pores with reduced strength and higher porosity than the lower w/c ratio. The additional material has improved the porosity compared to the CEM I due to increased hydration products, namely C-S-H gel, being formed within the capillary pores. From a practical perspective, given that the ternary combinations are comparable with the CEM I for both strength and porosity by 90 days at the

higher w/c ratio it would make them worthy of greater consideration if they were to also meet with additional criteria depending of the location and exposure conditions for the structure's location.

An increase in replacement level to 55% gives a greater difference in results whilst the strength-porosity relationship is still seen within the specific, individual combination mixes as shown in Figure 5.17.

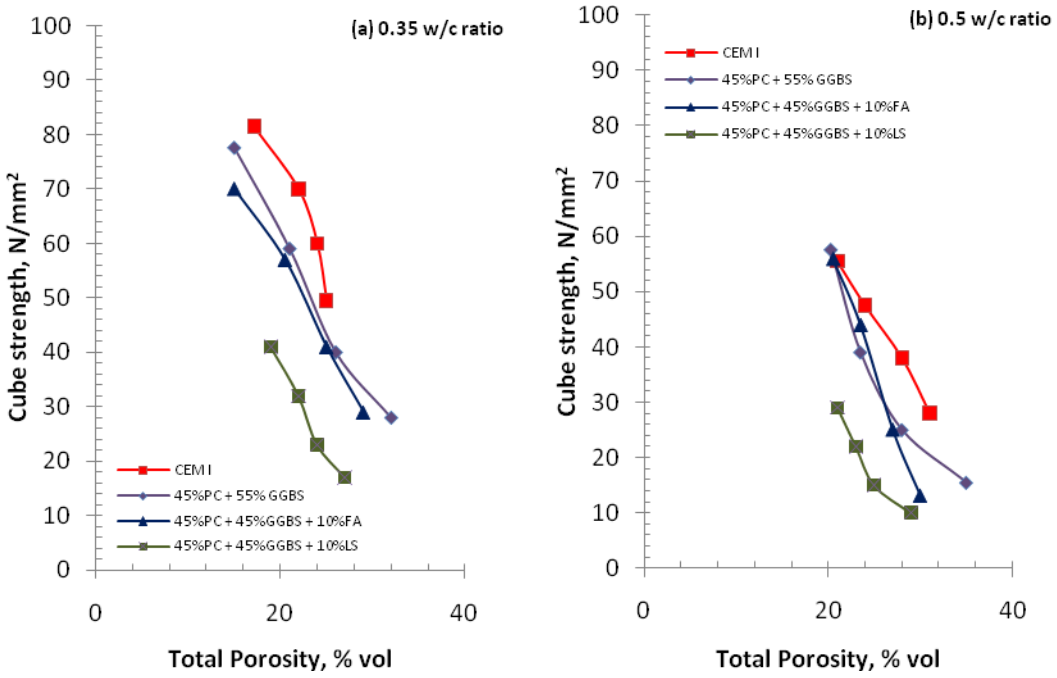


Fig 5.18: Cube strength aginast total porosity at the 55% replacement level

The 10% limestone ternary concrete may be disregarded with pore results, higher porosity and lower strength for both w/c ratios as its effectiveness as an inert filler are no longer apparent as they were at the lower replacement levels. At the lower w/c ratio the 10% fly ash does not give as high strength results by 90 days as the CEM I or the binary concrete, but its porosity is lower and the strength recorded is still sufficient for consideration in a practical context. The lower porosity may bring with it additional benefits that may well mean that a slightly lower strength is worth a trade-off for better permeation and durability; these will be

discussed in subsequent chapters. Certainly, with an increase to 0.5 w/c ratio the 10% fly ash is comparable with the CEM I and binary concretes.

5.9 Summary

In this chapter the strength properties were discussed in relation to the effects of the ternary additions. Overall it was seen that an increase in w/c ratio reduced the compressive strength of the concretes.

As the GGBS levels increased, the strength decreased due to the slower reaction of GGBS. However, longer-term strength gain was improved for the 35% GGBS level, which exceeded that of CEM I concrete. For the 55% and 75% levels a lower w/c ratio was necessary for this effect to have occurred by 180 days.

At the 35% GGBS level the addition of fly ash and limestone was of little benefit to the concretes, indeed, at the lower w/c ratio a negative effect was seen. With regards to the fly ash, its inclusion created competition with the GGBS for the free lime being produced by the hydrating CEM I. The limestone created a diluting effect, reducing the volume of active materials within the concrete. Increases in w/c ratios improved the ternary concretes relative to the CEM I, indicating the importance of the greater availability of water within the mix for the reaction of the ternary materials, but at 0.5 w/c ratio the strength was still lower than the 0.35 w/c ratio mixes.

The addition of ternary materials to the concretes did show an increased rate of early strength development for the 75% GGBS level at the higher w/c ratios where the early strength was seen to be higher than the binary concretes.

It was found that in order for all concretes to reach an equivalent strength of 40 N/mm^2 by 28 days varying w/c ratios would be required. In general it was found that the lower w/c ratio would be needed for the binary mixes compared to the CEM I concretes, illustrating further the different rate of strength development and the effects of w/c ratio.

Further, it was found that when each combination was viewed independently, though the concrete strength increased with that of the cement paste counterpart, the increase was dependant on both the additional material and level of replacement. Concurring with previous studies (*Kearsley & Wainwright, 2002; Kumar & Bhatacharjee, 2003; Mehta & Montiero, 2004*) a relationship between strength and porosity was found for the selected samples tested with the 10% fly ash ternary mix giving comparable results to that of the CEM I by 90 days for both replacement levels at 0.5 w/c ratio.

CHAPTER SIX: ABSORPTION & CAPILLARY RISE

6.1 Introduction

The previous chapter discussed the possible strength-porosity relationship seen in concrete, introducing the effects of porosity and the pore structure within the concrete matrix. Whilst strength plays an important role in the overall durability of concrete, the latter is a function of permeation properties and is dependent therefore, on the ease at which a gas or liquid can migrate through concrete. It is therefore the microstructure of both the cement paste and the paste-aggregate interfacial zone that are influential (*Garboczi, 1990* and *Basheer et al, 2005*), both of which are dynamic and change with time and environmental conditions. This chapter will examine the absorption characteristics of the test concretes by measuring initial surface absorption and sorptivity. These indicate the ability of concrete to take in a liquid and will be examined in relation to additional properties including porosity and compressive strength.

Within the hydrated cement paste are three main pore types: gel pores, capillary pores and air voids. Pipilikaki & Beazi-Katsioti (*2009*) distinguish the types of pores found within the microstructure. Those greater than 10,000 nm are air voids, or entrained air. Capillary pores can be one or two orders of magnitude greater than gel pores and represents spaces not filled by solid components of the hydrated cement paste (*Pipilikaki & Beazi-Katsioti, 2009*). The size of capillary pores depends on the distance between un-hydrated cement particles and the degree of hydration. It is the type and size of the pores within the microstructure of the concrete that affects transportation processes. Large capillaries, or macro-pores, range in size from 50 to 10,000 nm and it is these pores that have greatest impact on the transportation processes. Medium capillaries, or micro-pores, have sizes from 10 to 50 nm and gel pores from 2.5 to 10 nm, the former of which influence permeation. The gel pores are the interlayer spaces in the C-S-H but do not contribute significantly to the absorption of water due to their small size, they are generally about 3nm in diameter. Table 6.1, extracted from Mindess et al (*2003*),

classifies pores according to size and form of water within the pore together with the property that is generally affected.

Table 6.1: Pores within the concrete matrix (Mindess et al, 2003)

Name			Diameter	Role of Water	Affected Properties
Micro-pores "inter layer"	Gel Pores		Up to 0.5 nm	Structural water involved in bonding	Shrinkage, creep at all relative humidity
Micro-pores			0.5nm to 2.5nm	Strongly adsorbed water; no menisci form	Shrinkage, creep at all relative humidity
Small (gel) capillaries		Capillary pores	2.5nm to 10nm	Strong surface tension forces generated	Shrinkage between 50% and 80% relative humidity
Medium capillaries			10nm to 50nm	Moderate surface tension forces generated	Strength, permeability, shrinkage at high relative humidity, >80%
Large capillaries			50nm to 10µm	Behaves as bulk water	Strength, permeability
Entrained air			0.1mm to 1mm	N/A	Strength

The porosity of concrete is defined by Neville (*1995*) as the total volume of pores larger than the gel pores which will include capillary pores, both macro and micro. It is suggested by Mehta & Monteiro (*2006*) that a cement paste with a low w/c ratio will have micro-pores, whilst higher w/c ratios produce capillary pores as large as 3 to 5 µm. Entrapped or entrained air can both cause air voids, while capillary pores are generally irregular in shape, these are normally spherical (*Mehta & Monteiro, 2006*). Due to their size they are also capable of adversely affecting the strength of concrete. The critical pores size refers to the most frequently occurring diameter that allows maximum percolation of fluids through cement paste (*Winslow & Diamond, 1970*).

Within the microstructure itself, the interfacial zone is said to be the most porous and weaker and will therefore give the least resistance to any migrating gases or liquids. This zone can be as much as 33-50% of the total volume of the hardened cement paste (*Basheer et al, 2009*). In addition to these voids, an interlayer space exists within the C-S-H and whilst Powers (*1958*) suggested that it accounts for 28% porosity in the solid C-S-H, Feldman & Beaudoin

(*1976*) stated that this interlayer space can vary from 5 to 25Å, consequently it is too small to significantly impact the permeation of concrete.

6.2 Absorption Tests

All concrete mixes were tested for both initial surface absorption (ISAT) and capillary rise. The former is a standard test carried out in accordance with BS 1881: Part 206-1996 and data from this was supplemented by sorptivity results from the capillary-rise tests. Lea (*1998*) stated that absorption by any concrete, regardless of the mix, is a function of the drying temperature and immersion duration. In order to control these variables standard test procedures are necessary and hence the methodology outlined in Chapter 3 was adopted. It is worth noting that the preconditioning of the samples for each test differs. For the ISAT the concrete samples were oven dried to a constant weight unlike the samples for sorptivity tests that were unsaturated and air dried, prior to testing.

The initial surface absorption test (ISAT) is probably one of the most widely used tests (*Kumar & Bhattacharjee, 2002* and *Bungey, 1989*) enabling an assessment of the outer zone of concrete that offers protection to embedded steel. Whilst cover can be as much as 50mm the test tends to only cover the first few millimetres. The test measures uniaxial water penetration characteristics of a dry concrete surface under a low pressure of about 200mm head of water. The head of water is used as it provides conditions considered worse than the severest weather exposure created by heavy driving rain (*Kumar & Bhattacharjee, 2002*). The wetting of concrete surfaces from rain or splashing occur frequently due to capillary suction, e.g. in highway or coastal structures, thus making the transport of fluids through the material by this means, a primary parameter regarding the durability of any concrete. The absorption of water into the concrete can cause a number of problems. Solutes transported by the water can cause corrosion of reinforcement and water within the concrete can create freeze-thaw effects (*Neville, 1995*).

Whilst it is possible to carryout ISAT in-situ, tests are generally only carried out under laboratory conditions. The tests for this study were carried out in accordance with BS 1881:

Part 206:1996, as discussed in Chapter 3, at both 28 and 180 days. The test is applied to a single surface which makes it ideal for use as a non-destructive test as well as a laboratory permeation assessment and is derived from a method developed by Levitt's (1969) permeability tests for roofing tiles. The data is obtained by a force that is created as a result of the water surface tension within the capillary pores. As with all tests, the CEM I control mix provided a bench mark with which to compare the binary and ternary blends. It is also expected that the results will be indicative of the physical properties as well as the chemical effects of the binary and ternary materials such as the reactivity of the limestone and the delayed hydration of pozzolanic materials. Although the test is also carried at 30 and 60 minutes the calibrated ISAT-10 values are discussed as these adequately represent the absorption trends observed for all concrete samples across the range of w/c ratios and addition levels for both 28 and 180 day test ages. The data is discussed in relation to the void ratio and the w/c ratio in order to determine if a relationship exists and to observe any indication of the reactivity and physical properties of the materials used. Table 6.2 outlines the typical ISAT rankings or classifications for well cured concretes as per the Concrete Society (*1991*). These values have been indicated on the relevant charts to illustrate where the results lie with regards to these recommended values. Subsequent sections will look at the combined concrete mixes in relation to the activity of the ternary materials when they are examined in relation to the CEM I control mix, compressive strength and critical pore size.

Table 6.2: Typical ISAT values of well-cured oven dried concrete (Concrete Society,1991)

	ISAT ml/m²/s		
	10min	30min	60min
High	>0.50	>0.35	>0.20
Average	0.25-0.50	0.17-0.35	0.10-0.20
Low	<0.25	<0.17	<0.10

In addition to ISAT, sorptivity tests were carried out to supplement the data. This test was also performed on selected cement paste samples, the results of which will be discussed in subsequent sections. Kelham (1988) suggests that sorption force is inversely proportional to

the pore diameter, effectively the smaller the pore diameter, then the higher the sorptivity. With this in mind the porosity of selected combinations will again be examined to test this theory in respect of the additions used. Matys & Ferraris (1997) state that the sorptivity coefficient is essential to predict the service life of a concrete structure and thus enable improvements to its performance. The test itself, according to Dias (2000), is more reflective of how concrete, in a practical environment, is penetrated by deleterious agents and water as it is tested in an unsaturated condition as opposed to the oven dried ISAT samples. The samples are tested under these conditions as the test measures the intake of water by capillary suction and this can only take place in a partially dry sample, sorption of water will not occur in either a completely dry sample or in a saturated one. The moisture condition is hard to control and hence the results can be prone to variability.

6.2.1 35% GGBS Level

At the 35% GGBS level, the binary mixes across the range of w/c ratios were comparable with the CEM I control mix at 28 and 180 days, as shown in Figure 6.1. The addition of 10% fly ash increased the ISAT-10 value across all w/c ratios marginally, while the 10% limestone was comparable with CEM I and slightly higher than the binary, but lower than the fly ash at 0.35 w/c ratio.

By 180 days the trend was the same but more noticeable, with improvements in all cases on the 28 day results. This may be due to the fly ash reacting poorly with the lower w/c ratio this is likely to be due to a higher quantity of cementitious materials resulting in less efficiency in terms of the actual quantity reacting. The binary concrete gave the lowest absorption of all mixes at this GGBS level which is comparable to the 10% limestone at the 0.35 w/c ratio. At the lower, 0.35 w/c ratio the sorptivity gave a similar trend as indicated in Figure 6.3, which was more noticeable and this appears to be the case across the range of w/c ratios in general. At 28 days at both 0.5 and 0.65 w/c ratios, the 10% fly ash ternary mix indicated higher sorptivity values but lower ISAT values. By 180 days these reduced and were consistent with the findings of the ISAT at this later test age but the differences for the fly ash concretes are relatively small.

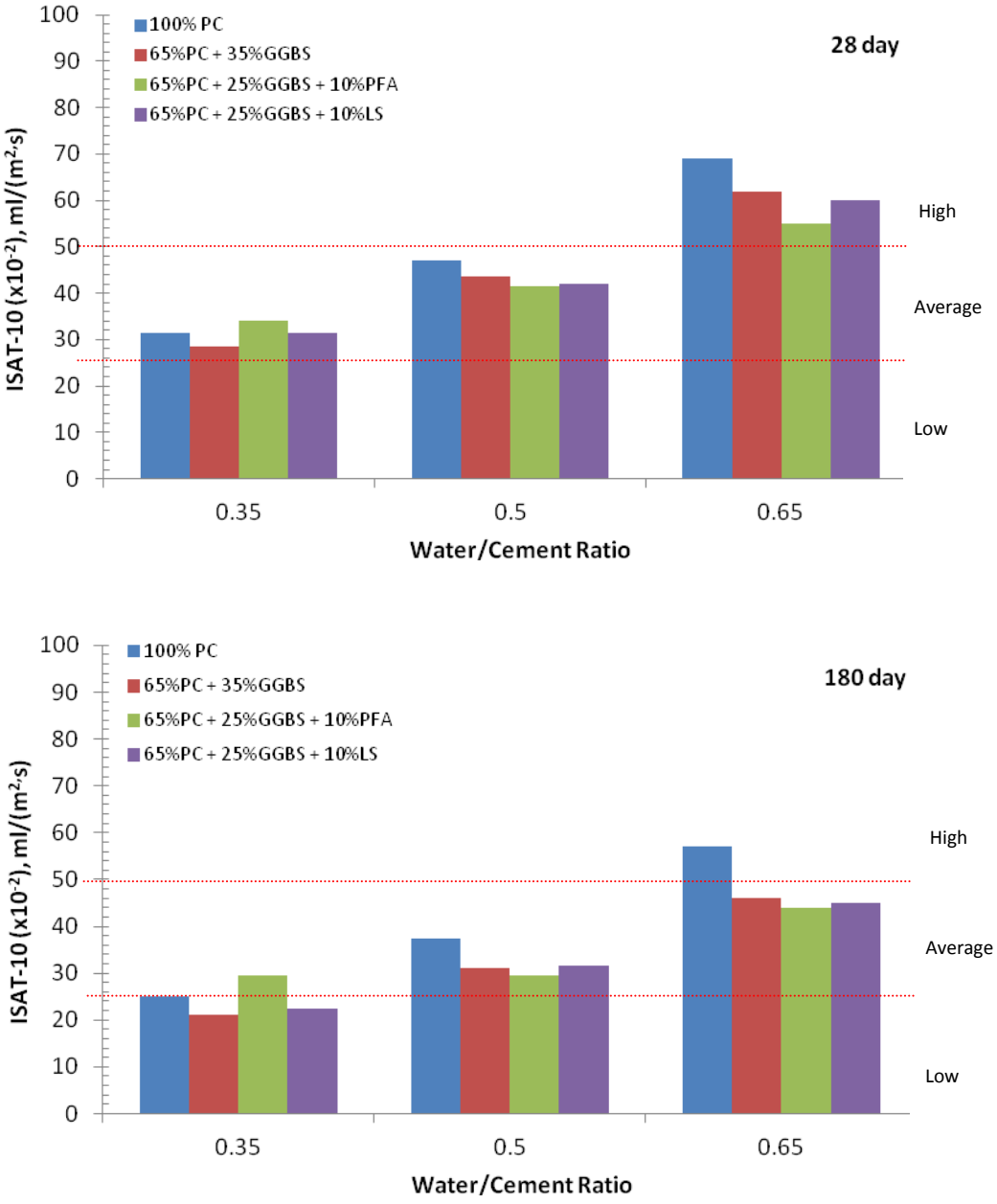


Fig 6.1: ISAT-10 indicating absorption across the range of water cement ratios at the 35% addition level.

It is unclear why this difference occurred, but it may have been due to the nature of the tests and possibly the preconditioning. The sorptivity test relies on the absorption of water through capillary rise and its calculation is determined on the weight of the specimen at given times. The base of the specimen sat in water to a depth of 3 to 5mm creating a larger area for absorption, compared to the ISAT test, where a limited area was subjected to a 200mm head of water. At an early age it may be that due to the slower reaction of both the GGBS and fly ash, as they compete for the lime hydration had slowed, with the higher w/c ratio more water is available from the mix filling the voids creating more voids when the specimen is dried.

At 0.5 w/c ratio, the ISAT trend at 28 and 180 days was the same as that of 0.35 w/c ratio. The CEM I concrete showed higher ISAT-10 values, whereas the binary mix was reduced and comparable with the 10% limestone ternary mix, with the 10% fly ash mix giving the lowest ISAT-10. The 0.65 w/c ratio gave the same trend as the 0.5 for both test ages, but with noticeably higher values.

When compared to the calculated voids ratio in Figure 6.2, the ISAT results show clearly that the binary and ternary mixes have a lower voids ratio than that of CEM I concretes across the range of w/c ratios. The fineness of the limestone aids in creating a denser microstructure as it is suggested that it is an inert filler and contributes little cementitiously (*Menendez et al, 2003*). It appears that it is the physical characteristics, as in the fineness, of the limestone that allows for improved initial surface absorption at the earlier (28 day) test age. At this time, the pozzolanic materials are likely to have limited contribution. By 180 days, pozzolanic reactivity has greatly increased, contributed to by the GGBS and the fly ash also to some extent, and thus the initial surface absorption is further improved.

The lower 0.35 w/c ratio indicate a reduced voids ratio for the binary and ternary mixes, suggesting a better packing density when compared to the CEM I. Except for the 10% fly ash which gave slightly higher results, as already discussed, the results are comparable. The voids ratio for the binary and ternary mixes was lower than CEM I across the range of w/c ratios, as expected. At 0.5 and 0.65 w/c ratios, the ISAT values of the ternary mixes were comparable and lower, respectively, than the binary and CEM I concretes. A similar trend

occurs at 180 days, but the 10% fly ash had improved to give lower results than its limestone counterpart. Whereas, the limestone acts as inert filler, the fly ash creates further pozzolanic reactions within the concrete, despite competition for the free lime with GGBS. Capillary pores have been reduced by the formation of secondary C-S-H as suggested by Ghrici et al (*2007*), thus reducing the ISAT.

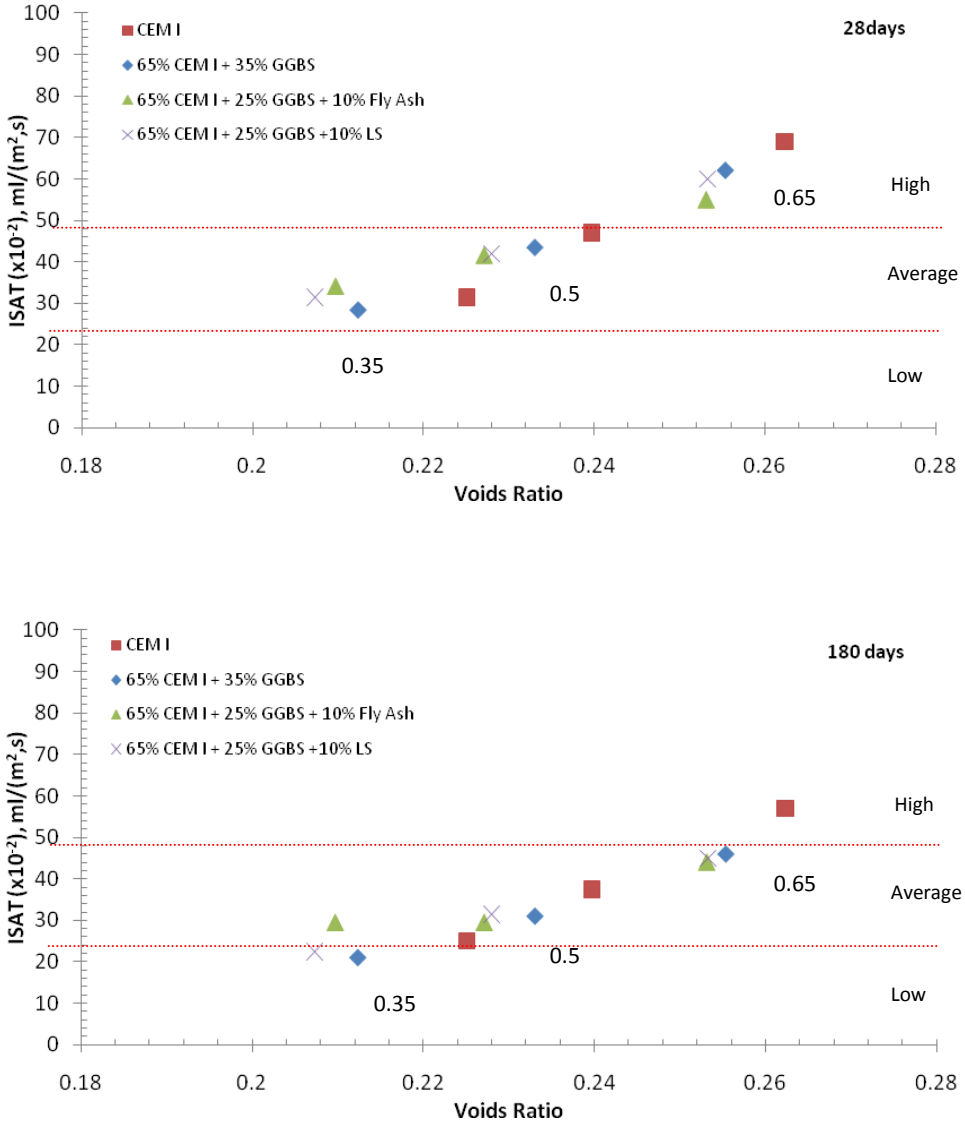


Fig 6.2: Comparison of ISAT-10 and voids ratio across the range of water cement ratios at the 35% addition level.

The ISAT tests were supported by the sorptivity tests, the results of which are shown in Figure 6.3. The binary mixes appear to give better sorptivity at the earlier 28 day test age but the later test age of 180 days indicates improvements, with the 10% fly ash at the higher w/c ratios giving better results. The reaction between the 10% fly ash and water gave reduced sorptivity, this may indicate that at the lower w/c ratio the fly ash acts more as an inert filler, hence the better results from the limestone than fly ash due to the limited lime available from the hydrating CEM I reacting with the GGBS. Although fixed at 165ml/m^3 there was more water in the mix, compared to the volume of materials, allowing for increased hydration products, thus more lime is available allowing both GGBS and fly ash to react. It was clear from the results that a 10% limestone addition had no significant effect in reducing the sorptivity further than achieved with the binary mix when compared to CEM I concrete. This was also noted with the ISAT results and suggests that for absorption properties, at this GGBS level, the limestone makes little contribution although its value as an inert filler has been noted (*Ramezanianpour et al, 2009*).

Ghrici et al (*2007*) studied the effects of limestone with CEM I and a natural pozzolana sourced from the Beni-Saf quarry in western Algeria. As with the results from this study these authors reported that a reduction in w/c ratio decreased the sorptivity of the mixes (their study included 0.4 and 0.6 w/c ratio) and this was further reduced over time. The effect of w/c ratio was further indicated when a 15% limestone binary mix was tested. In this case, the mix was comparable with the CEM I mix at the 0.6 w/c ratio at 28 days and slightly reduced by 180 days. The lower w/c ratio had the effect of reducing the sorptivity value significantly although it remained higher than the natural pozzolana binary and ternary mixes. Indicating that when used alone, limestone is not as effective as when used with an additional material at higher w/c ratio. Tsivilis et al (*2003*) found similar effects and stated that a 15% addition of limestone at a high w/c ratio had little effect on the sorptivity of concrete.

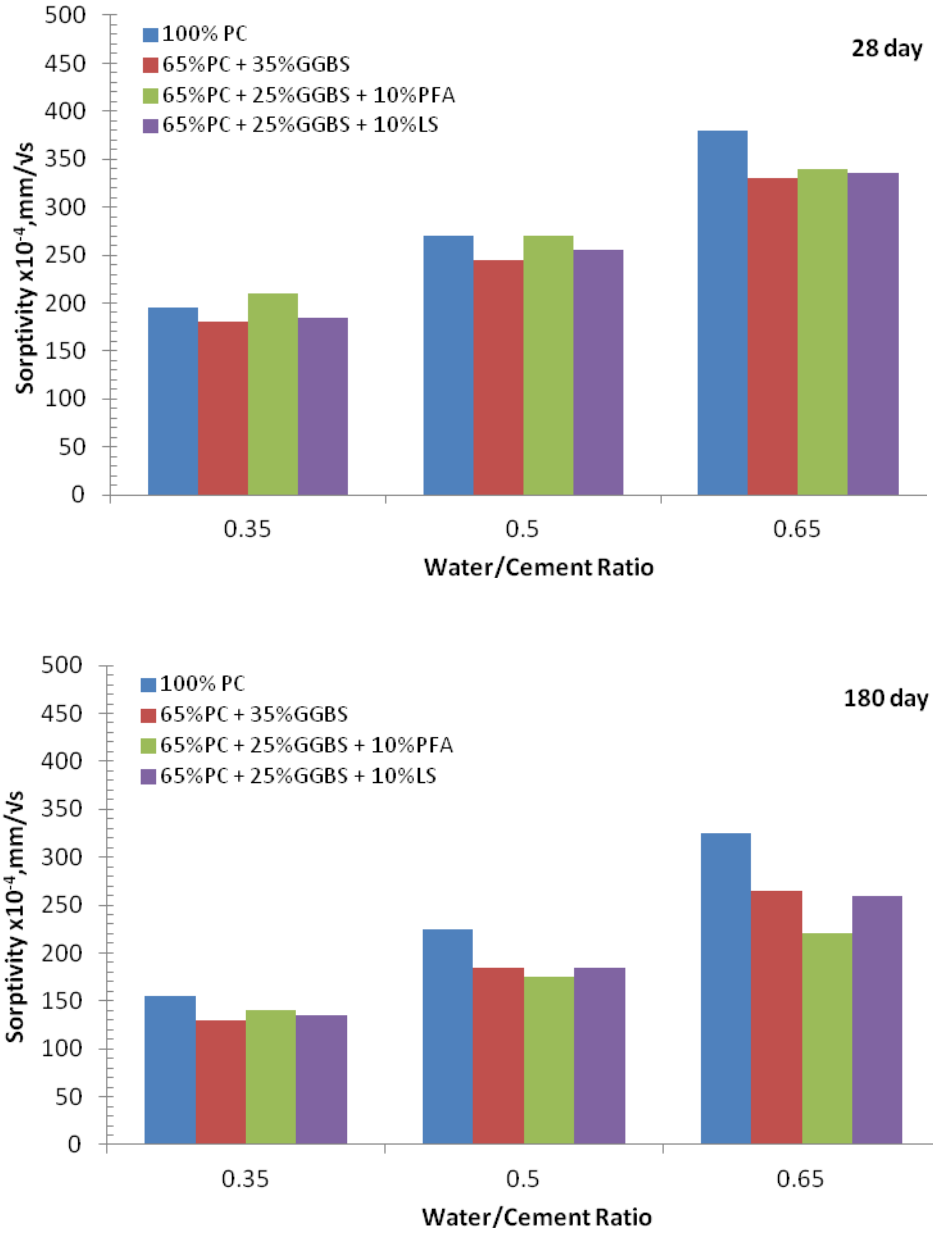


Fig 6.3: Sorptivity of 35% GGBS level concretes

6.2.2 55% GGBS Replacement Level

Figure 6.4 shows that for the 55% GGBS level the binary mixes were marginally lower when compared to the CEM I mix at the 0.35 and 0.5 w/c ratios, with a greater difference noted at 0.65 w/c ratio. At 28 days, the ternary mixes gave much higher ISAT values than both the binary and CEM I concretes. The fly ash and limestone additions were comparable at 0.5 w/c ratio, with the fly ash mix showing slightly higher results at 0.35 w/c ratio. For both 0.35 and 0.5 w/c ratios, the 10% fly ash gave lower ISAT values than the 20% fly ash. With an increase to 0.65 w/c ratio, this reversed with 20% fly ash giving lower values than 10% with the former comparable with the 10% limestone ternary. Given that the difference in these mixes was the w/c ratio and the level of aggregates, it may be that the increase in w/c ratio has a positive effect in improving the reactivity of the fly ash. A greater volume of aggregates would create greater ITZ which can result in increased porosity so this is not the likely cause.

At the 0.65 w/c ratio, the volume of cementitious materials is lower and the volume of CEM I hydrating will produce limited lime, available to react with both the GGBS and fly ash, increasing competition between them compared to the lower addition level. At the lower and mid range w/c ratio, it would appear that the reaction is slower and competition is higher, and more water has aided the reaction of the materials having the effect of producing more C-S-H to fill the pores thus reducing ISAT values for the 20% level replacement. However, whether this reduction is as a result of the GGBS or the fly ash reaction is unclear, they react differently but compete for the same hydration product for activation, the free lime.

By 180 days, the ISAT values reduced, due to a greater level of reaction across the range of w/c ratios and combinations, as expected, but the levels of improvement differ as shown in Figure 6.4. An increase from 0.35 to 0.5 w/c ratio shows all mixes to be lower than CEM I, with the 10% fly ash giving a slightly lower ISAT value than the others. With a further increase to 0.65 w/c ratio, a more noticeable reduction was observed for the binary and ternary concretes compared to CEM I, indicating further reaction attributed to GGBS. The 20% fly ash is comparable with the binary mix, but there was little difference between any of these mixes.

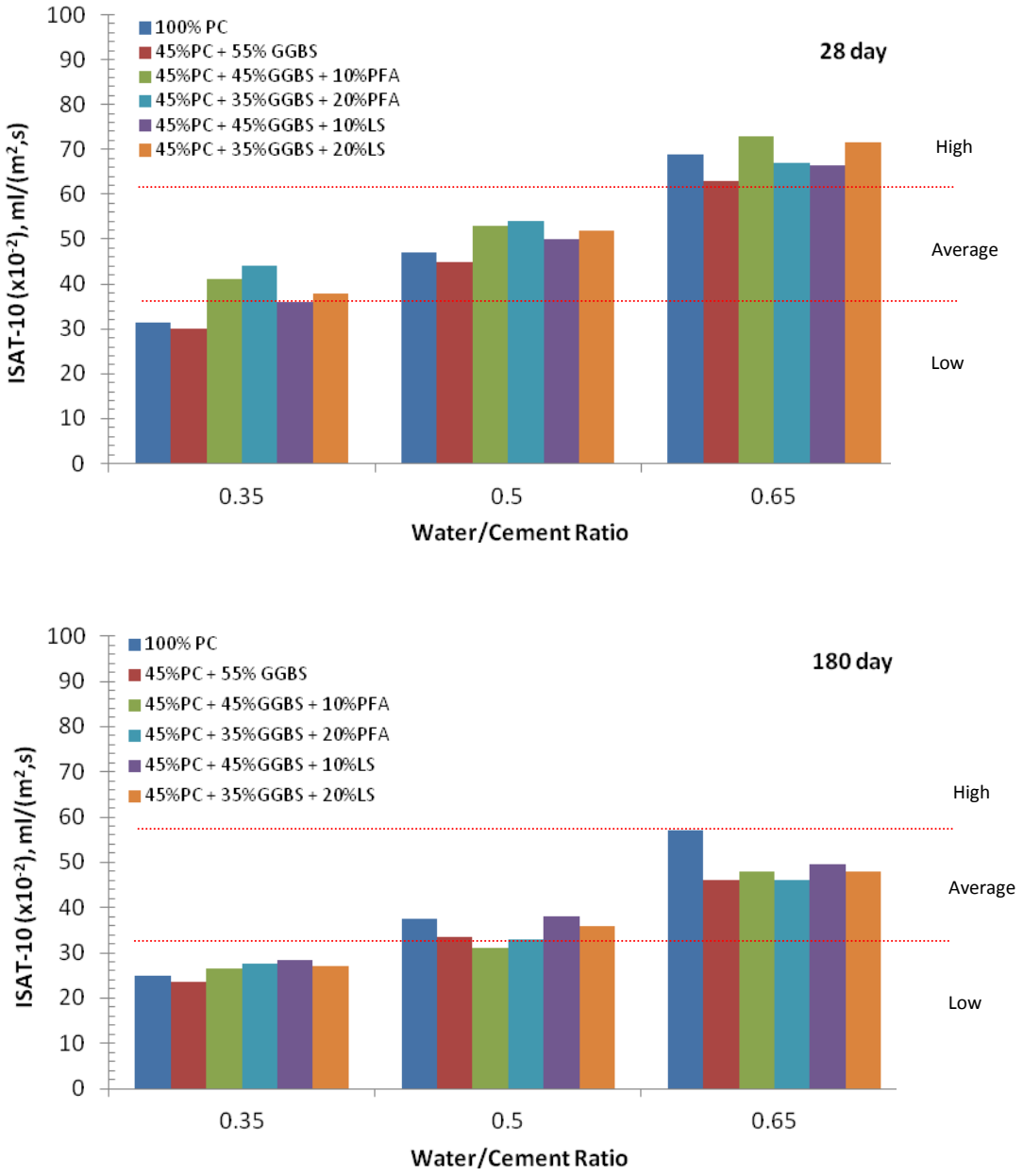


Fig 6.4: ISAT-10 indicating absorption across the range of water cement ratios at the 55% addition level.

As seen at the 35% level, the decrease in voids ratio with the additional material does not necessarily correspond to the ISAT values. Figure 6.5 compares the voids ratio and the ISAT values at the 55% GGBS level, which indicates that at the lower 0.35 w/c ratio, whilst the binary mix gave an ISAT value comparable to the CEM I concrete with a lower voids ratio, the ternary mixes gave increased values, with both 10% and 20% fly ash giving the highest results at this w/c ratio.

The increase in w/c ratio to 0.5 gave higher ISAT values, as expected with the binary mix still comparable to CEM I. The ternary mixes were higher but had similar values. A further increase to 0.65 w/c ratio gave improved ISAT values for the 20% fly ash and 10% limestone ternary compared with the other ternary mixes. Despite this, the values were still “high” ISAT values at this test age. A longer curing period of 180 days improved the ISAT values across the range of mixes and w/c ratios, with the majority falling within the average ranking but it is clear that the voids ratio does not relate to the ISAT values.

Whilst voids ratio is calculated based on the mix design, it is more appropriate to consider the actual measured critical pore diameter of the cement paste, and the developed microstructure. Transport of water through concrete depends on the porosity of the capillaries, as previously discussed and the connectivity and pore structure also affects the transportation of water (*Ramezanianpour et al, 2009*) which are influenced by the w/c ratio and degree of hydration.

The effect of w/c ratio on the ISAT values was noticeable with regard to the effect of the additions. It would appear that this can be attributed to the disconnection of pores at the lower to mid range w/c ratio. With an increase to 0.65 w/c ratio Irassar (*2009*) states that capillary disconnection is harder, the capillary pores are more connected allowing water to be absorbed more readily. By 180 days, with the extended period, the binary and ternary mixes have produced more C-S-H to fill the voids within the microstructure, thus aiding in the disconnection of the capillary pores.

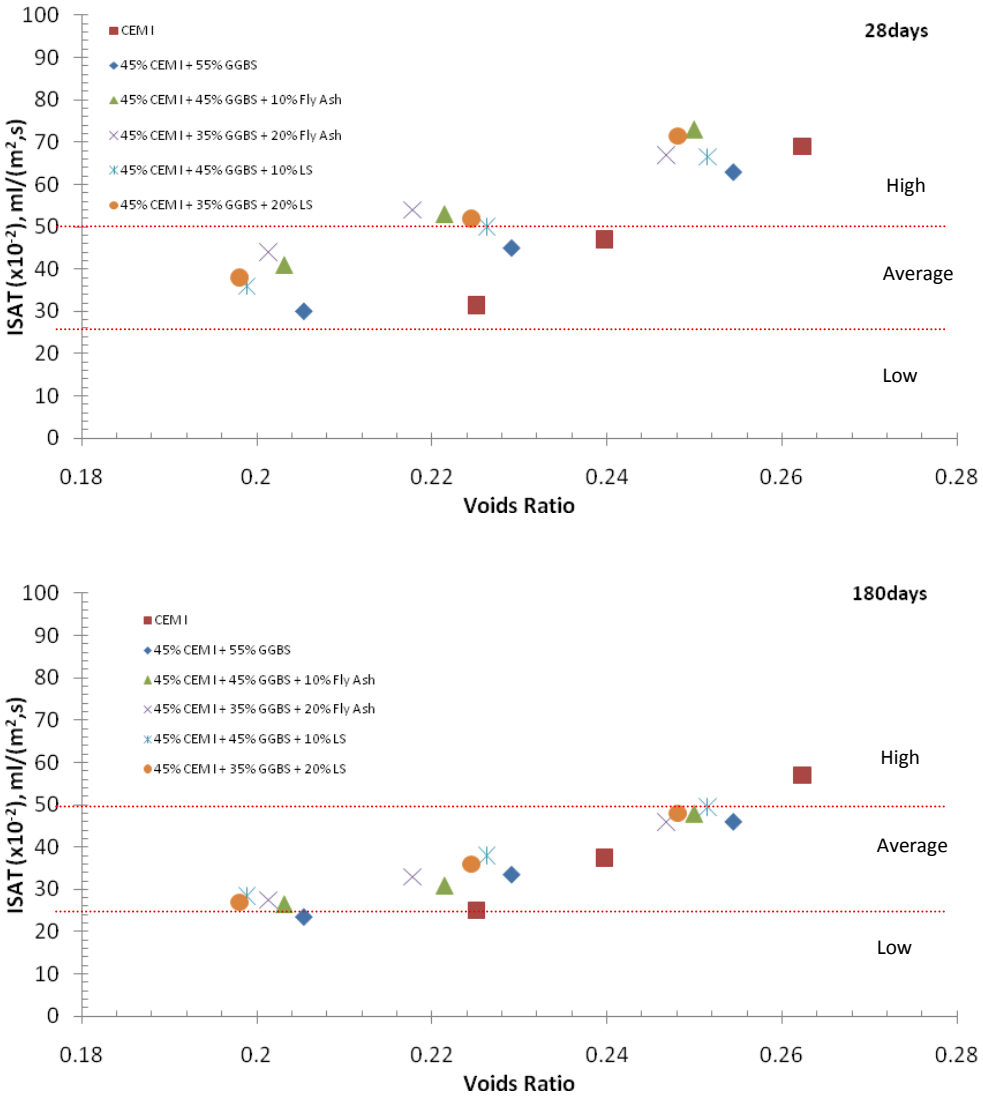


Fig 6.5: ISAT-10 against void ratio across the range of water cement ratios at the 55% addition level.

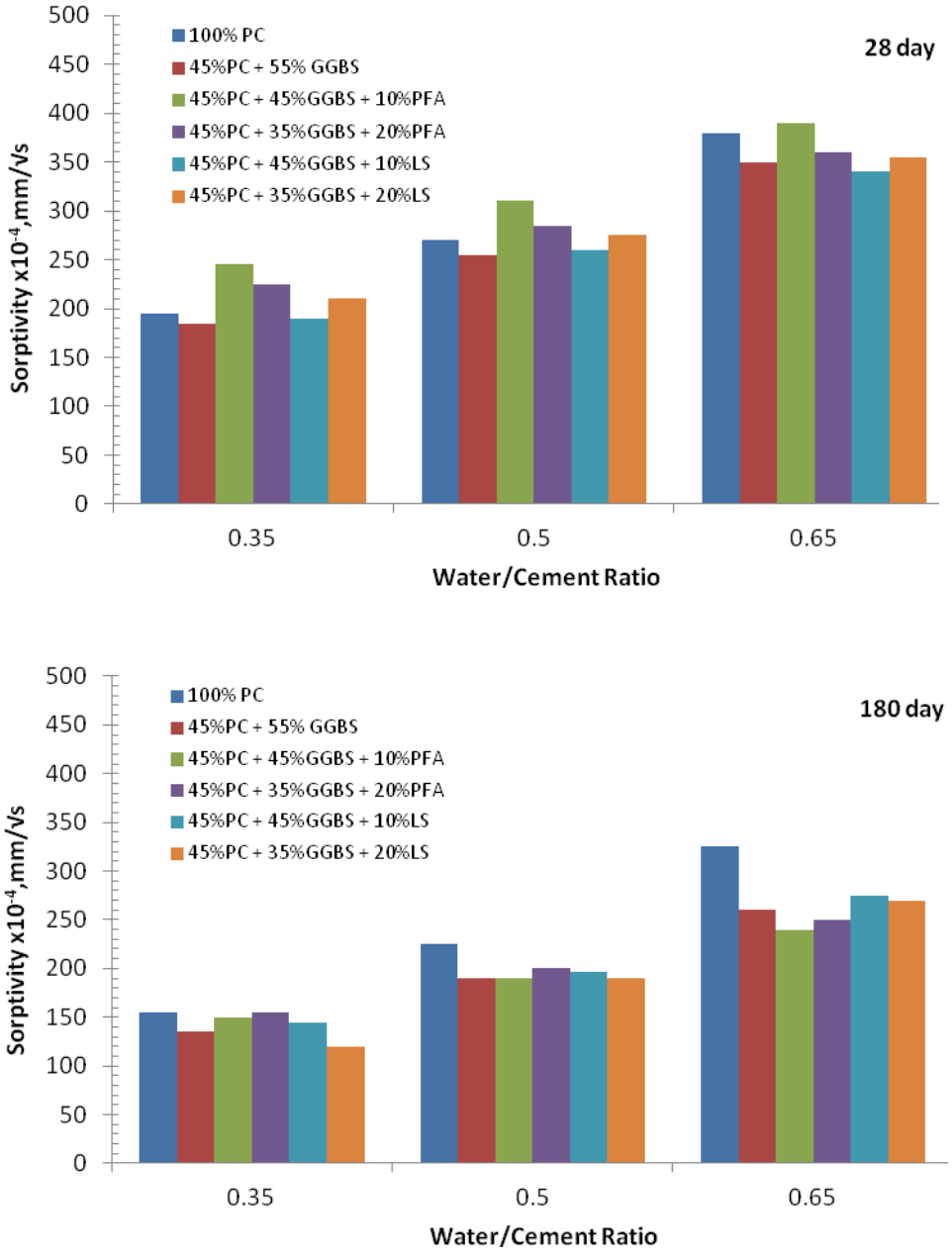


Fig 6.6: Sorptivity of 55% GGBS level concretes

6.2.3 75% GGBS Level

Figure 6.7 shows the ISAT results for the 75% GGBS level. At 28 days, the CEM I control mix gave the lowest value, compared with the binary and ternary mixes, across the range of w/c ratios. At the 0.65 w/c ratio, the 10% fly ash ternary concrete was comparable with that of CEM I. The binary mix was higher than CEM I concrete, but gave lower absorption than the ternary mixes at 0.35 and 0.5 w/c ratios and, at 0.65 w/c ratio, was marginally higher than that with 10% fly ash (the only ternary concrete that improved compared to the binary mix). When compared to the ISAT values, the sorptivity tests indicate different behaviour. The higher fly ash level in the ternary concrete gave improved sorptivity at 28 days, as shown in Figure 6.8. The 10% fly ash was equal to the binary mix and the 20% fly ash lower, though still higher than CEM I at the 0.35 w/c ratio. An increase in w/c ratio reduced the sorptivity of both these mixes considerably compared to their counterparts at the 55% replacement level as shown in Figure 6.10.

By 180 days, the CEM I concrete remained low for both 0.35 and 0.5 w/c ratios, whilst the 0.35 w/c ratio mixes with 10% limestone ternary mixes gave the lowest ISAT results, marginally lower than the CEM I. At 0.5 w/c ratio, this ternary blend concrete was much higher, whilst the 10% fly ash ternary mix was only slightly higher than the CEM I. At 0.65 w/c ratio, the 10% limestone ternary mix again was the lowest and comparable with the binary.

A similar pattern was seen at 180 days for the fly ash concretes but age certainly improved the effects of the limestone at 0.35 and 0.5 w/c ratios. This may suggest that the limestone is either acting as an inert filler more effectively in the remaining pores after hydration (although this is not seen so obviously in other tests), or may not be as inert as initially believed and contribute to the reactivity of the combined materials (*Ramezanianpour et al, 2009*). These concretes are seen to be comparable if not lower than all other mixes. For the mixes with the 0.65 w/c ratio, the 10% limestone ternary concrete had the lowest sorptivity, the additional two limestone ternary concretes (20% and 35%) were higher than the fly ash ternaries but still comparable with the CEM I and binary concretes. The CEM I control shows little improvement in sorptivity with time (Figure 6.8), so it is evident that additions,

such as GGBS, PFA and limestone, are effective after prolonged curing and indeed improve the porosity of concrete over a period of time.

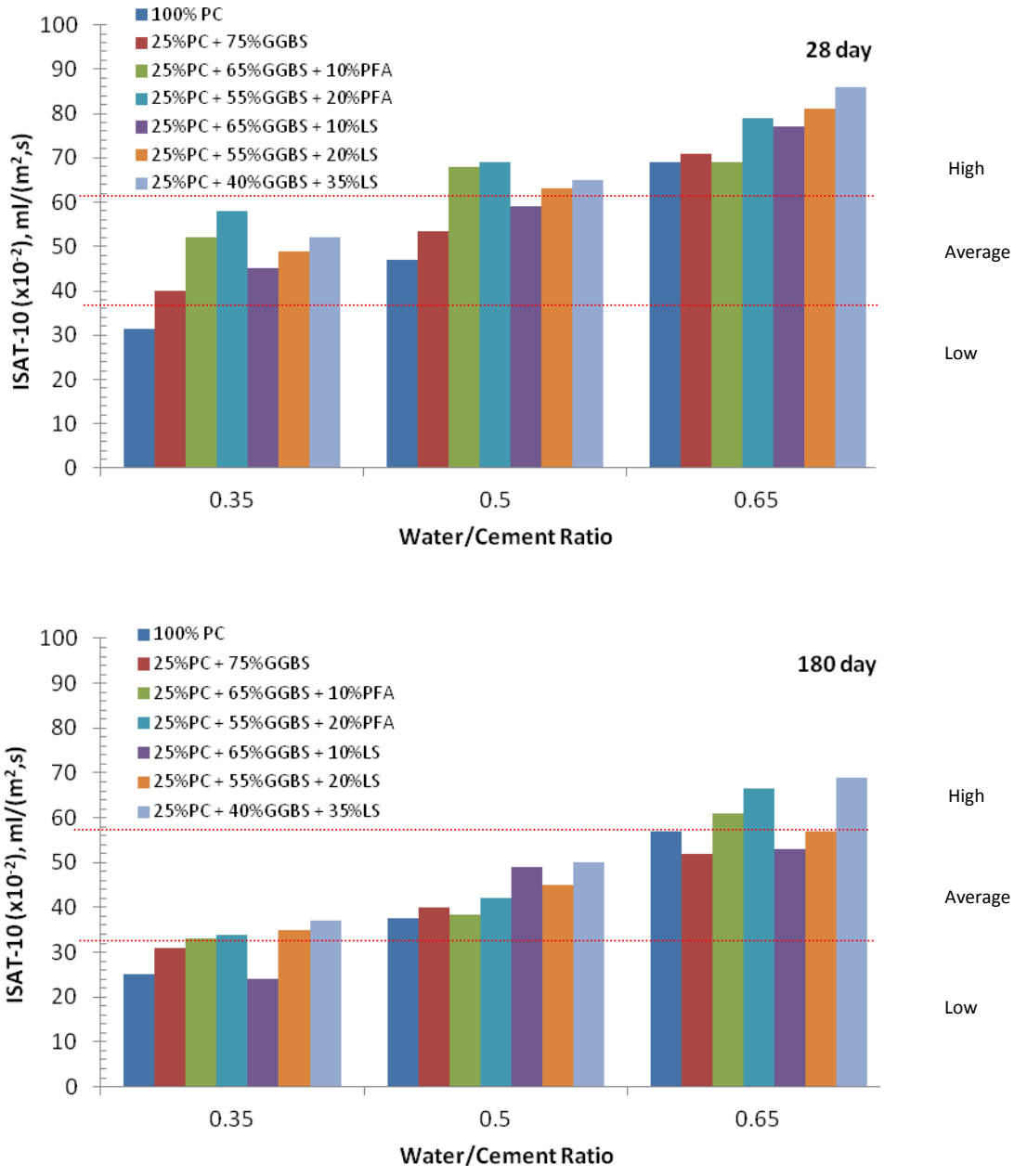


Fig 6.7: ISAT-10 indicating absorption across the range of water cement ratios at the 75% addition level.

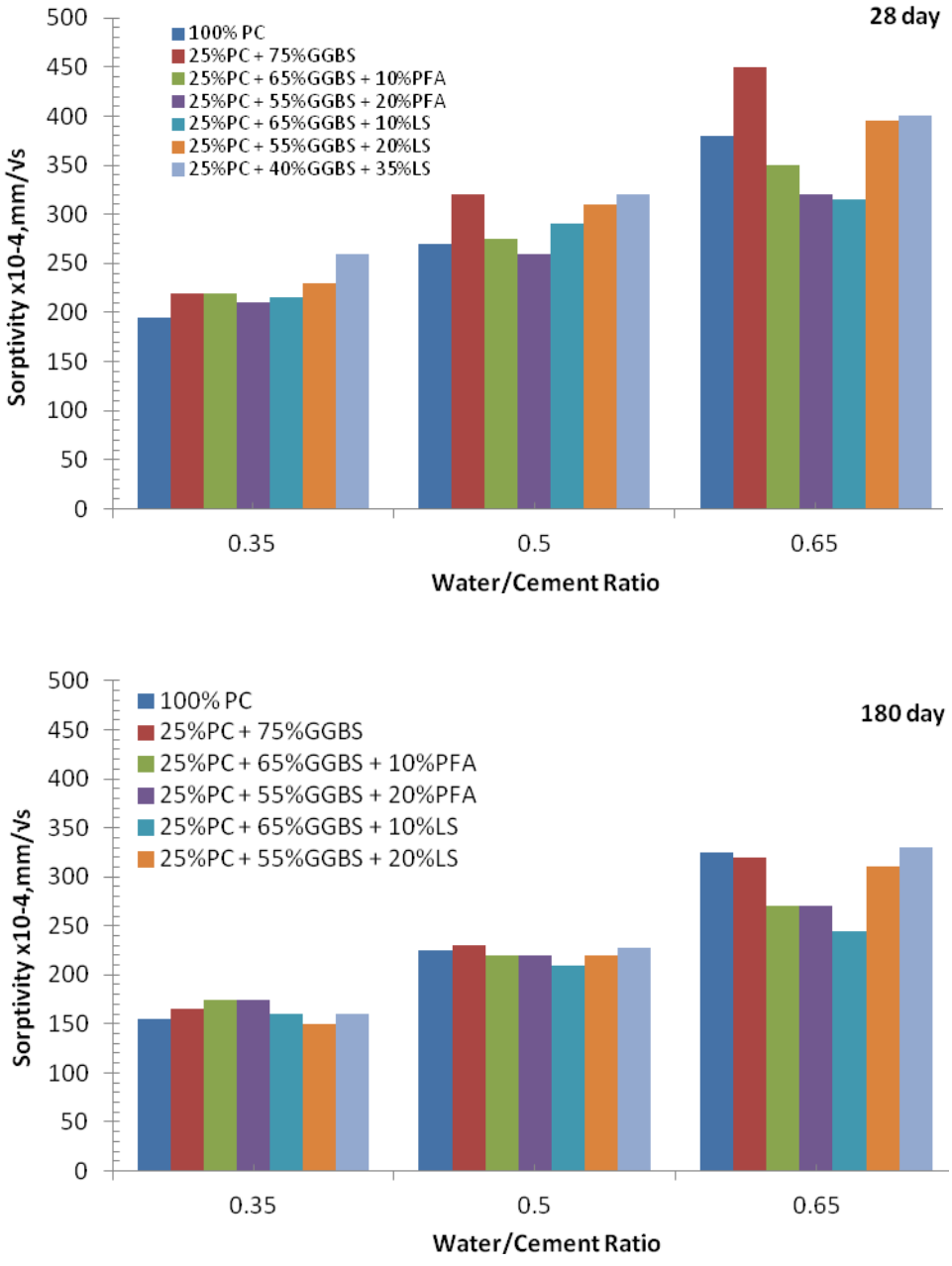


Fig 6.8: Sorptivity of 75% GGBS level concretes across the range of w/c ratios

The effect of increased volumes of limestone increasing sorptivity corresponds with other studies on its use as a binary material. Ramezanianpour et al (*2009*) reported that whilst w/c ratio had the effect of decreasing sorptivity with reducing quantities of limestone, increasing limestone content gave greater sorptivity as suggested by Tsivilis et al (*1999*). The limestone, due its fineness, acts as filler in the pore spaces between the aggregate and cement paste and pores in the bulk paste and with an increase in addition level the average particle size reduces, making the limestone less effective as filler as a wall effect is created (*Tasdemir, 2003; Guemmadi et al, 2009*).

The fly ash relies on the initial hydration of the CEM I to produce free lime to enable pozzolanic reactions, together with the alkalis. The GGBS requires this same product, in addition to alkalis to activate the reaction, and thus competes with the fly ash for the lime, as noted above. Given the significantly reduced sorptivity it may indicate that the fly ash is reacting with the GGBS in some way due to the lower volume of CEM I producing limited amounts of lime, which is being used by the higher volume of GGBS. During the hydration of GGBS alkalis are released progressively with more GGBS, this is likely to be increased and may account for the reaction of the fly ash as the increased alkalinity of the pore water aids in the breakdown of the glass material in the fly ash. Whilst the GGBS requires the same breakdown of glass by the hydroxyl ions released by the CEM I during its hydration, it releases additional alkalis.

At the higher GGBS level it is clear that at 28 days the volume of additions requires significantly more time to produce hydration products to fill the capillary pores within the structure of the concrete. As stated previously, the lower voids ratio for the binary and ternary mixes is calculated and it should be noted that the extent of reaction at 28 days is not considered, indeed the calculation assumes the voids ratio of a dry mix and does not consider the effects of hydration products following the addition of water. By 180 days, the effect of the fly ash as a pozzolanic material is evident as the initial surface absorption has decreased. Yet whilst it is generally believed that a low voids ratio, indicating denser packing, impedes the ingress of water, it is evident in Figure 6.9 that the increase in limestone to 35%, despite giving a lower calculated void ratio, results in the higher ISAT value by 180 days. This clearly indicates

that it is the reactivity of the material that is important and whilst packing is a physical effect, reactivity is more dominant in relation to concrete structure development.

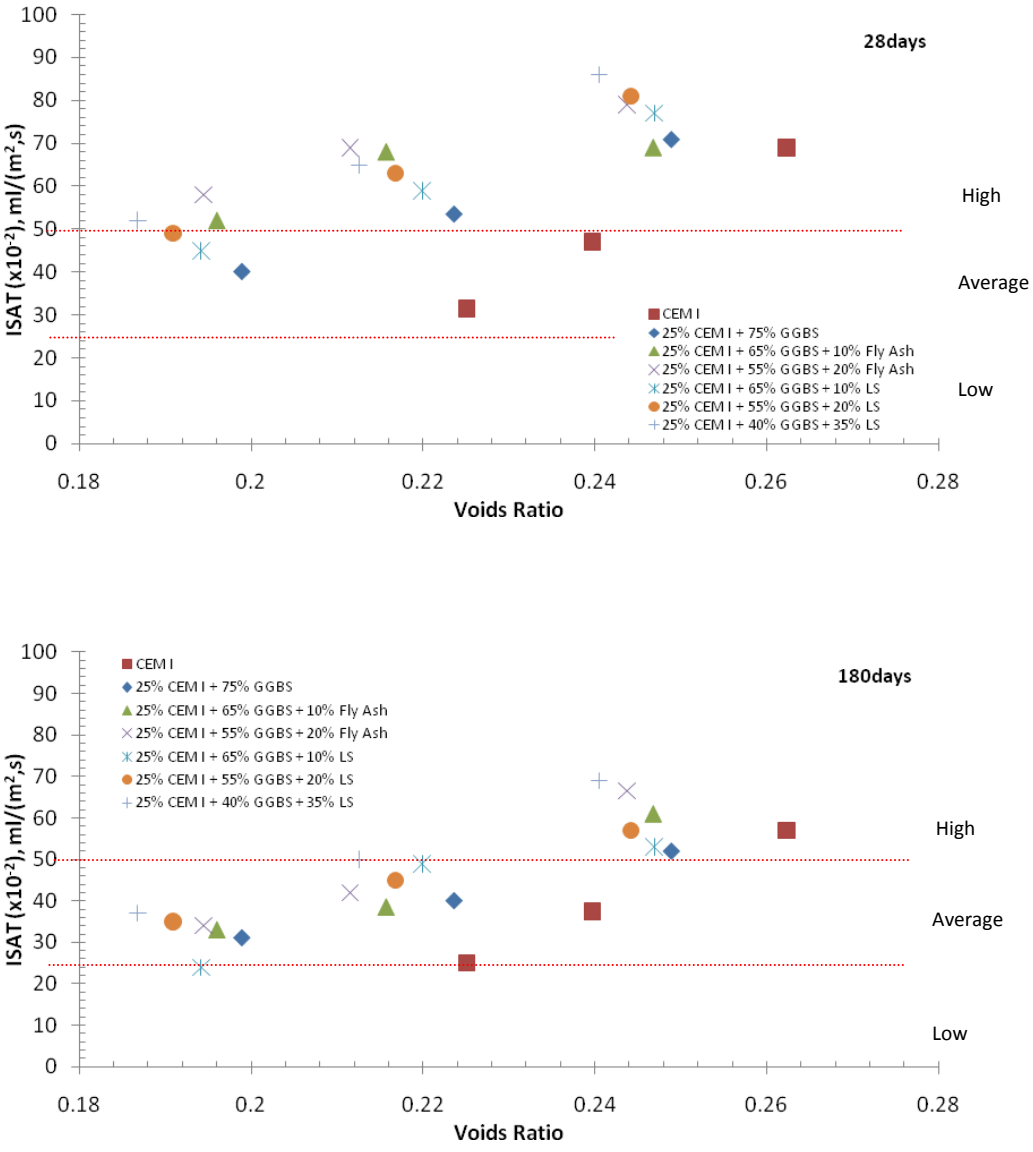


Fig 6.9: ISAT-10 against void ratio across the range of water cement ratios at the 75% addition level.

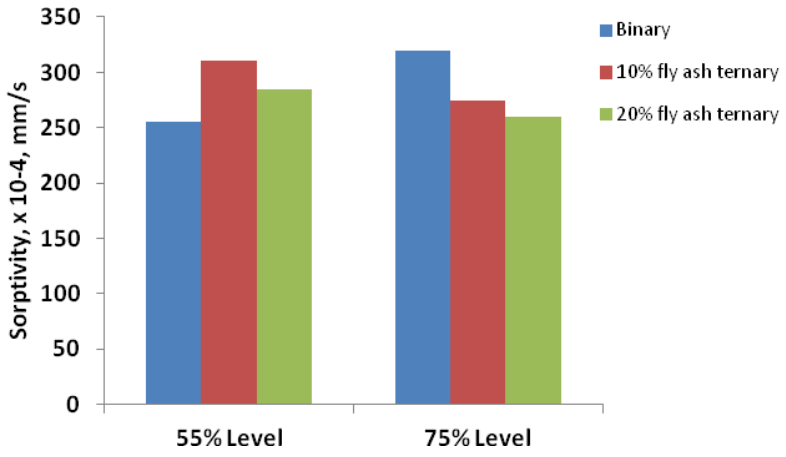


Fig 6.10: Sorptivity of 55% and 75% GGBS level binaries and fly ash ternary mixes at 0.5 w/c ratio

6.3 Effects of Combined Additions

There is little in the literature that discusses the effects of cement combinations in relation to many of the tests carried out in this study, indicating the need for such a holistic examination into the properties of additions such as fly ash and limestone as ternary materials. Comparisons can be drawn with regards to the effects of binary materials as there are numerous studies reviewing the effects of GGBS, fly ash and limestone in this respect. Table 6.3 indicates the ISAT -10 values of all samples tested across the range of w/c ratios and gives the relative results as percentages of the CEM I control mix. Table 6.4 provides a similar comparison for the sorptivity data. Overall, the effect is that ISAT and sorptivity are reduced generally for the higher w/c ratio across the range of combinations compared to the CEM I control and this is more noticeable at 180 days. This is likely to be due to the reduction in cement paste. The cement paste, contained within the concrete matrix, is a network of pores as previously discussed.

Table 6.3: ISAT-10 data and relative results as a percentage of CEMI control

Mix Combination	ISAT-10			
	x10^{-2} ml/m^2,s		% of CEM I	
	28	180	28	180
0.35 w/c ratio				
CEM I	31	25	100	100
65%PC + 35%GGBS	29	21	90	84
65%PC + 25%GGBS + 10%FA	34	30	108	118
65%PC + 25%GGBS + 10%LS	32	23	100	90
45%PC + 55% GGBS	30	24	95	94
45%PC + 45%GGBS + 10%FA	41	27	130	106
45%PC + 35%GGBS + 20%FA	44	28	140	110
45%PC + 45%GGBS + 10%LS	36	29	114	114
45%PC + 35%GGBS + 20%LS	38	27	121	108
25%PC + 75%GGBS	40	31	127	124
25%PC + 65%GGBS + 10%FA	52	33	165	132
25%PC + 55%GGBS + 20%FA	58	34	184	136
25%PC + 65%GGBS + 10%LS	45	24	143	96
25%PC + 55%GGBS + 20%LS	49	35	156	140
25%PC + 40%GGBS + 35%LS	52	37	165	148
0.5 w/c ratio				
CEM I	47	38	100	100
65%PC + 35%GGBS	44	31	93	83
65%PC + 25%GGBS + 10%FA	42	30	88	79
65%PC + 25%GGBS + 10%LS	42	32	89	84
45%PC + 55% GGBS	45	34	96	89
45%PC + 45%GGBS + 10%FA	53	31	113	83
45%PC + 35%GGBS + 20%FA	54	33	115	88
45%PC + 45%GGBS + 10%LS	50	38	106	101
45%PC + 35%GGBS + 20%LS	52	36	111	96
25%PC + 75%GGBS	54	40	114	107
25%PC + 65%GGBS + 10%FA	68	39	145	103
25%PC + 55%GGBS + 20%FA	69	42	147	112
25%PC + 65%GGBS + 10%LS	59	49	126	131
25%PC + 55%GGBS + 20%LS	63	45	134	120
25%PC + 40%GGBS + 35%LS	65	50	138	133
0.65 w/c ratio				
CEM I	69	57	100	100
65%PC + 35%GGBS	62	46	90	81
65%PC + 25%GGBS + 10%FA	55	44	80	77
65%PC + 25%GGBS + 10%LS	60	45	87	79
45%PC + 55% GGBS	63	46	91	81
45%PC + 45%GGBS + 10%FA	73	48	106	84
45%PC + 35%GGBS + 20%FA	67	46	97	81
45%PC + 45%GGBS + 10%LS	67	50	96	87
45%PC + 35%GGBS + 20%LS	72	48	104	84
25%PC + 75%GGBS	71	52	103	91
25%PC + 65%GGBS + 10%FA	69	61	100	107
25%PC + 55%GGBS + 20%FA	79	67	114	117
25%PC + 65%GGBS + 10%LS	77	53	112	93
25%PC + 55%GGBS + 20%LS	81	57	117	100
25%PC + 40%GGBS + 35%LS	86	69	125	121

Table 6.4: Sorptivity data and relative results as a percentage of CEMI control

Mix Combination	Sorptivity			
	x10^{-4}, mm/$\sqrt{s}$		% of CEM I	
	28	180	28	180
0.35 w/c ratio				
CEM I	195	155	100	100
65%PC + 35%GGBS	180	130	92	84
65%PC + 25%GGBS + 10%FA	210	140	108	90
65%PC + 25%GGBS + 10%LS	185	135	95	87
45%PC + 55% GGBS	185	135	95	87
45%PC + 45%GGBS + 10%FA	245	150	126	97
45%PC + 35%GGBS + 20%FA	225	155	115	100
45%PC + 45%GGBS + 10%LS	190	145	97	94
45%PC + 35%GGBS + 20%LS	210	120	108	77
25%PC + 75%GGBS	220	165	113	106
25%PC + 65%GGBS + 10%FA	220	175	113	113
25%PC + 55%GGBS + 20%FA	210	175	108	113
25%PC + 65%GGBS + 10%LS	215	160	110	103
25%PC + 55%GGBS + 20%LS	230	150	118	97
25%PC + 40%GGBS + 35%LS	260	160	133	103
0.5 w/c ratio				
CEM I	270	225	100	100
65%PC + 35%GGBS	245	185	91	82
65%PC + 25%GGBS + 10%FA	270	175	100	78
65%PC + 25%GGBS + 10%LS	255	185	94	82
45%PC + 55% GGBS	255	190	94	84
45%PC + 45%GGBS + 10%FA	310	190	115	84
45%PC + 35%GGBS + 20%FA	285	200	106	89
45%PC + 45%GGBS + 10%LS	260	197	96	88
45%PC + 35%GGBS + 20%LS	275	190	102	84
25%PC + 75%GGBS	320	230	119	102
25%PC + 65%GGBS + 10%FA	275	220	102	98
25%PC + 55%GGBS + 20%FA	260	220	96	98
25%PC + 65%GGBS + 10%LS	290	210	107	93
25%PC + 55%GGBS + 20%LS	310	220	115	98
25%PC + 40%GGBS + 35%LS	320	227	119	101
0.65 w/c ratio				
CEM I	380	325	100	100
65%PC + 35%GGBS	330	265	87	82
65%PC + 25%GGBS + 10%FA	340	220	89	68
65%PC + 25%GGBS + 10%LS	335	260	88	80
45%PC + 55% GGBS	350	260	92	80
45%PC + 45%GGBS + 10%FA	390	240	103	74
45%PC + 35%GGBS + 20%FA	360	250	95	77
45%PC + 45%GGBS + 10%LS	340	275	89	85
45%PC + 35%GGBS + 20%LS	355	270	93	83
25%PC + 75%GGBS	450	320	118	98
25%PC + 65%GGBS + 10%FA	350	270	92	83
25%PC + 55%GGBS + 20%FA	320	270	84	83
25%PC + 65%GGBS + 10%LS	315	245	83	75
25%PC + 55%GGBS + 20%LS	395	310	104	95
25%PC + 40%GGBS + 35%LS	400	330	105	102

By examining the data in respect of the w/CEMI ratio rather than w/c ratio ("c" being the combined cementitious materials), it is possible to examine the effects of the fly ash and limestone when they are added to the GGBS binary mix. The effect may be positive, indicated below the trend line of the binary mix, or negative, indicated above the line, depending on the property. The effects of the ternary additions at 28 days for both ISAT and sorptivity across the range of w/CEMI ratios are shown in Figures 6.11 to 6.13. At the lower w/CEMI ratio, shown in Figure 6.11, it is clear that the ternary mixes have a negative effect on the ISAT value at 28 days across the range of addition levels. At the lower 35% addition level, both the ternary concrete were higher than the binary but remained lower than the ternary concretes for the other two addition levels (55% and 75%). Contrary to the ISAT values the sorptivity results showed a positive effect, albeit marginal, for the 10% fly ash.

An increase in w/c ratio to 0.5 gave a more positive result for the lower level of GGBS, shown in Figure 6.12. The filler effect of the limestone addition was more positive at the lower 35% addition level with the increase in w/c ratio. The fly ash reaction was also positive though both of them were marginal. The increasing GGBS levels did not benefit from the addition of the ternary materials. Again the sorptivity values followed a similar trend to that of the lower w/c with the ternary mixes at the higher addition level, or w/CEMI+GGBS level, clearly showing a positive effect in reducing sorptivity. This effect was more noticeable with a further increase in w/c ratio to 0.65, shown in Figure 6.13. With regard to the ISAT values the 10% ternary additions indicate a positive improvement at the lower replacement level (35%) a marginal improvement was also seen with the 10% fly ash at the higher 75% replacement level.

It is clear that the ternary additions cause various effects at differing GGBS levels and w/c ratios. The limestone is generally considered to act as an inert filler as discussed previously and by Ramezanianpour et al, (*2009*), other studies are of the opinion that limestone can actually improve hydration by acting as an acceleration site (*Ramachandran & Zhang, 1986*). Given the findings of Nehdi et al (*1998*) that limestone, acting as filler, can reduce water demand and increase plasticiser efficiency, this certainly seems to support the results of the lower w/c ratio mixes containing limestone.

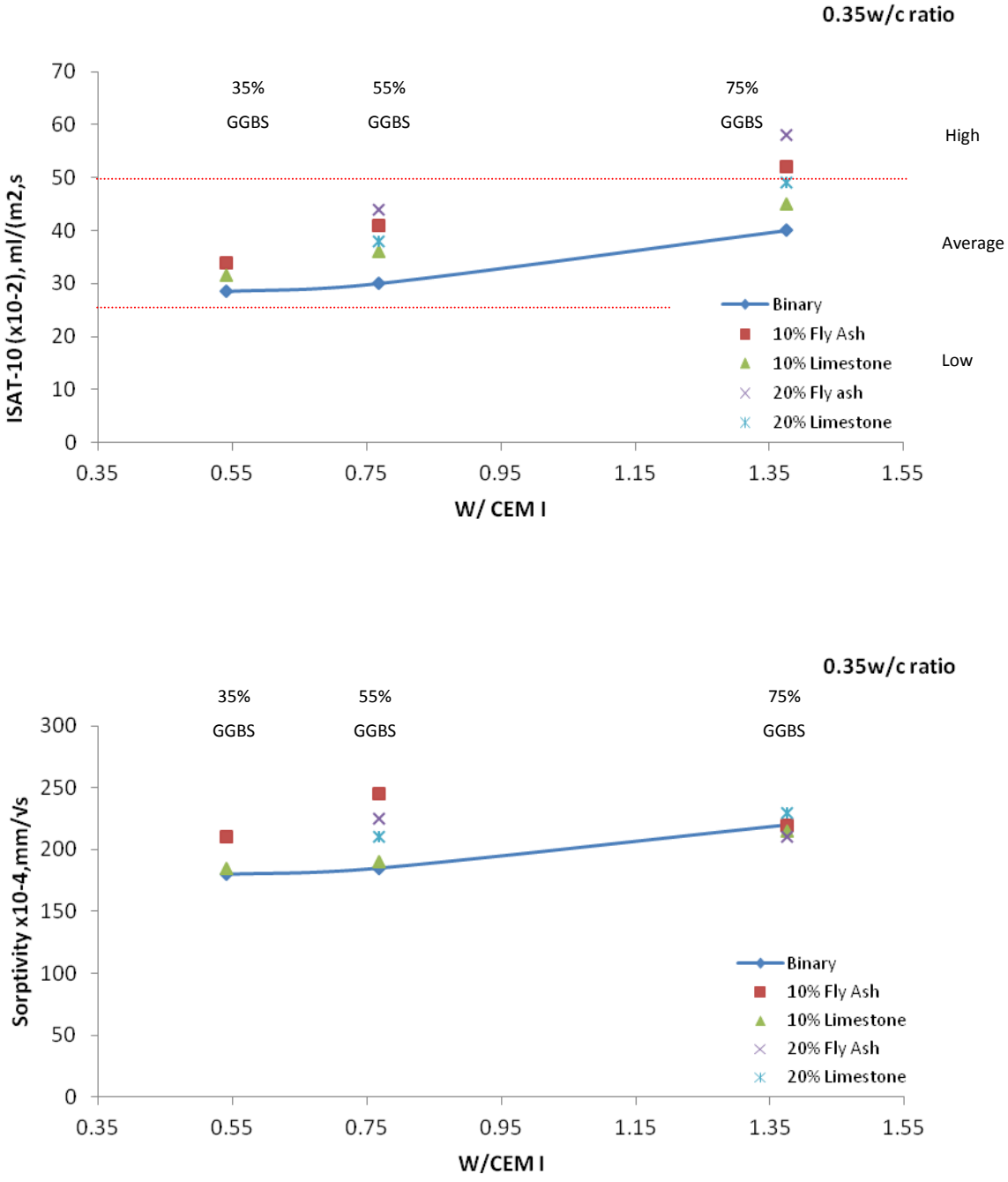
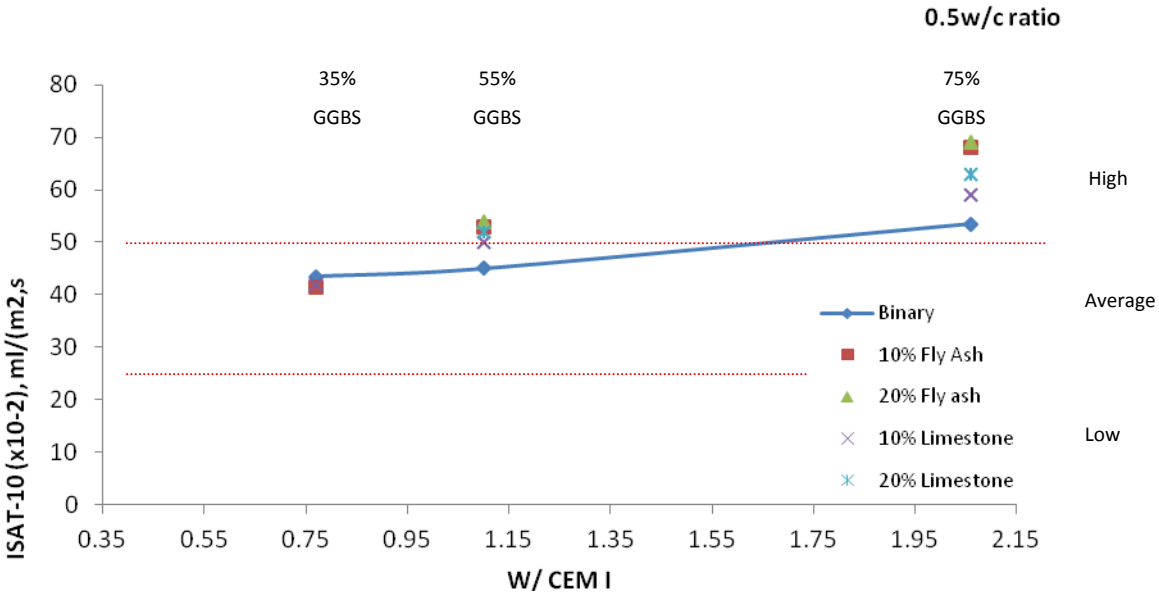


Fig 6.11: Effects of ternary materials at 0.35 w/c ratio.



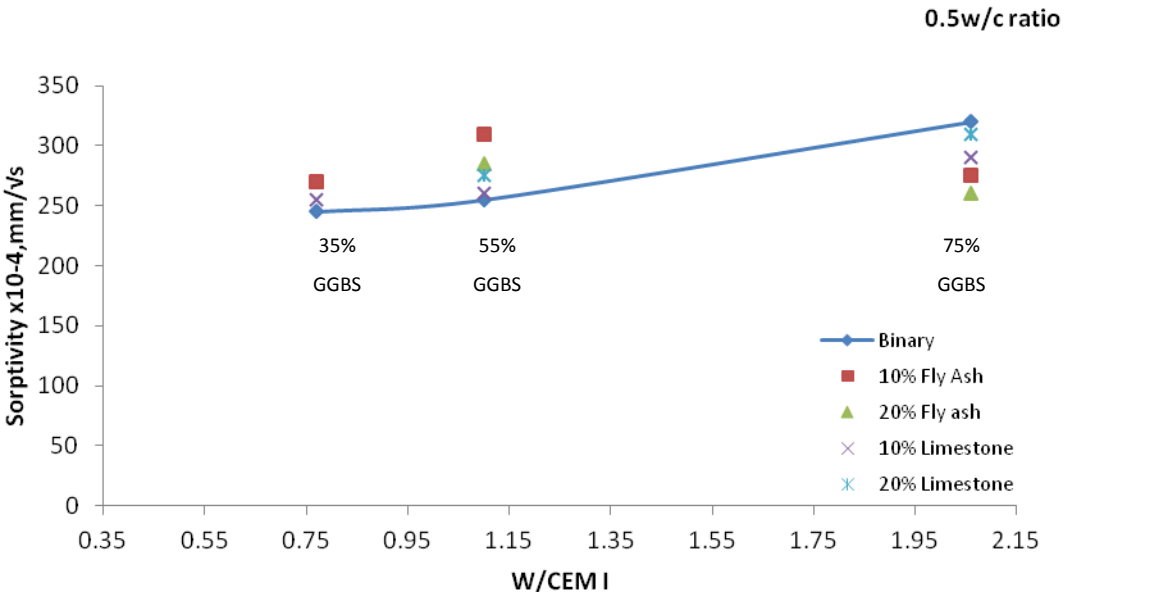


Fig 6.12: Effects of ternary materials at 0.5 w/c ratio at 28 days.

Water demand is further discussed by Tsivilis et al (*2002*). They studied limestone cements and found those containing 20% limestone to have lower water sorptivity thus indicating the positive effects of limestone and certainly support the positive effects seen with this study's limestone ternary concretes, exhibited at both test ages across the range of w/c ratios at both 35% and 55% addition levels. At the higher 75% addition level it appears that the limestone was more detrimental, possibly due to the filler effect and the higher volume of fines within the materials. The 75% addition level shows high absorption values for all ternary mixes at 28 days with a w/c ratio of 0.35 and the complete range of mixes at the mid-range and higher w/c ratios, CEM I and binary mixes included.

The fly ash gives low absorption values with prolonged curing and this is more evident at the 55% addition level. On the whole, the results of the fly ash concretes are comparable with the limestone ternary mixes, but given the difference in properties, both physical and pozzolanic, the reason for the improvements may also differ. The fly ash is slower to react than the CEM I, which is why prolonged curing to 180 days greatly improves the absorption value of these ternary mixes. The glass content within the fly ash may also have affected the rate of pozzolanic reaction, a higher pH of the pore water is necessary to aid the breakdown of this material to further increase the reaction products. However, the fly ash used for this study was Type S (conforming to BS EN 450-1 2005) and the glass content would not be that significant in relation to the reactivity. At the lower 35% replacement level this is not so noticeable but increases more so as the addition level rises indicating a diluting effect where there is less CEM I in the mix to aid in the initial reaction of both the GGBS and the fly ash.

Elahi et al (*2010*) found that a binary mix of 50% GGBS gave better sorptivity results at a 44 day test age than at 91 days, but by increasing the content to 70% this effect was reversed. Fly ash was also used as a binary material with 20% addition having no effect at 44 days but considerably decreasing sorptivity by 91 days. Sorptivity was increased at both test ages when the fly ash content was doubled to 40% when compared to CEM I. Whilst the test ages differ, some similarities can be drawn with Elahi et al's data in general, whereby the 55% binary mix is improved compared to CEM I as to did the 50% mix of Elahi et al (*2010*).

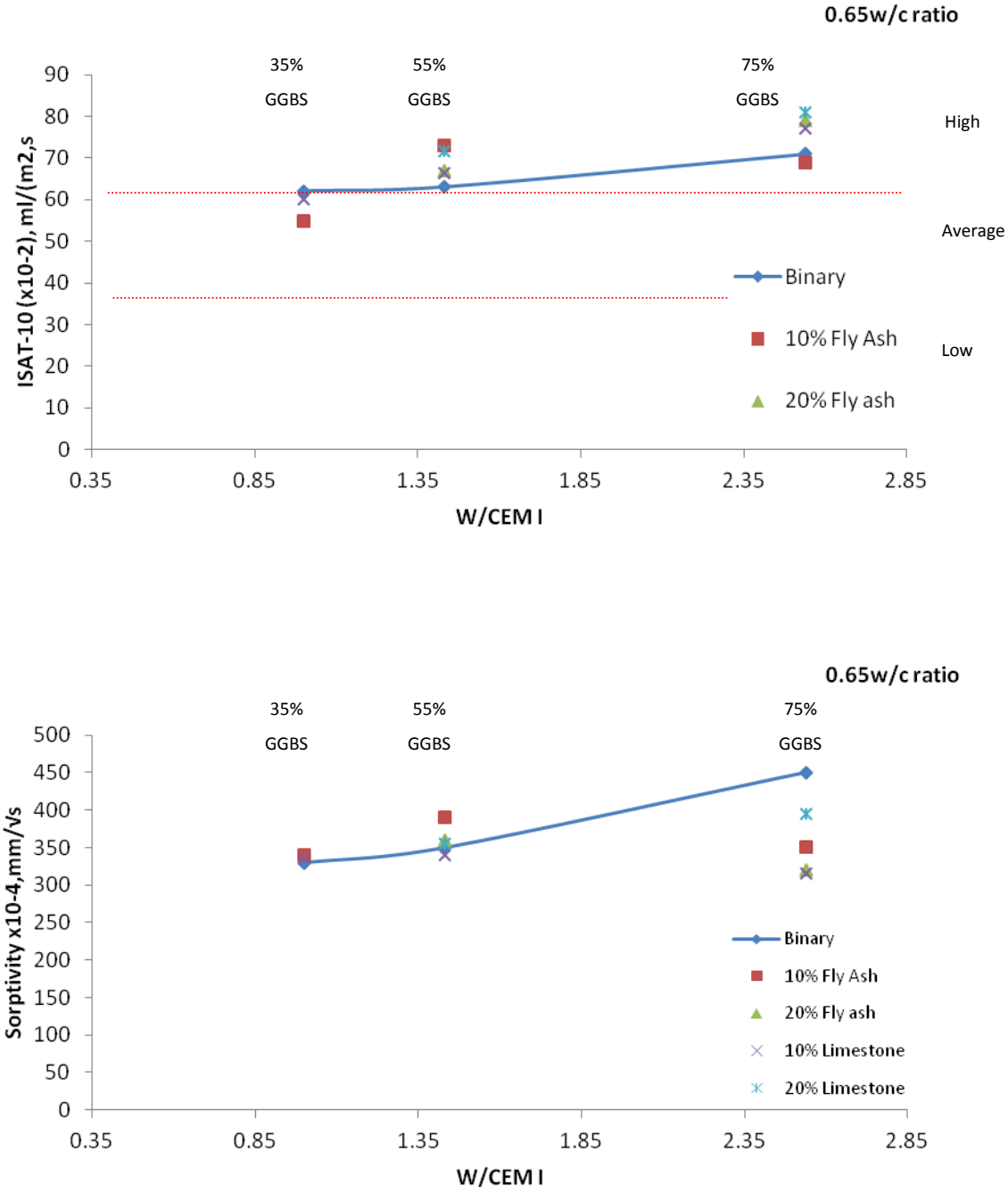


Fig 6.13: Effects of ternary materials at 0.65 w/c ratio.

6.4 Initial Surface Absorption and Cube Strength

Given that absorption is dependent on the continuity of the pore system and the network of pores within the concrete matrix, including those of the cement paste and the interfacial transition zone, it may be assumed that there would be some correlation between the data for the absorption tests and that of compressive strength for the tested samples. However, when plotted against compressive strength (Figure 6.14(a)) there is poor correlation, indicated by the R^2, across the range of w/c ratios at 28 days. At the later test age the mid-range w/c ratio gives a stronger correlation as shown in Figure 6.14(b). The R^2 value, or coefficient of correlation, is merely indicative of the prediction of future outcomes and is calculated based on the given results. The range will vary from 0.1 to 1.0 and criteria for interpretation is arbitrary but based on Buda & Jaynowski (*2010*) a small correlation is indicated at 0.1 to 0.3, medium 0.3 to 0.5 and strong 0.5 to 1.0.

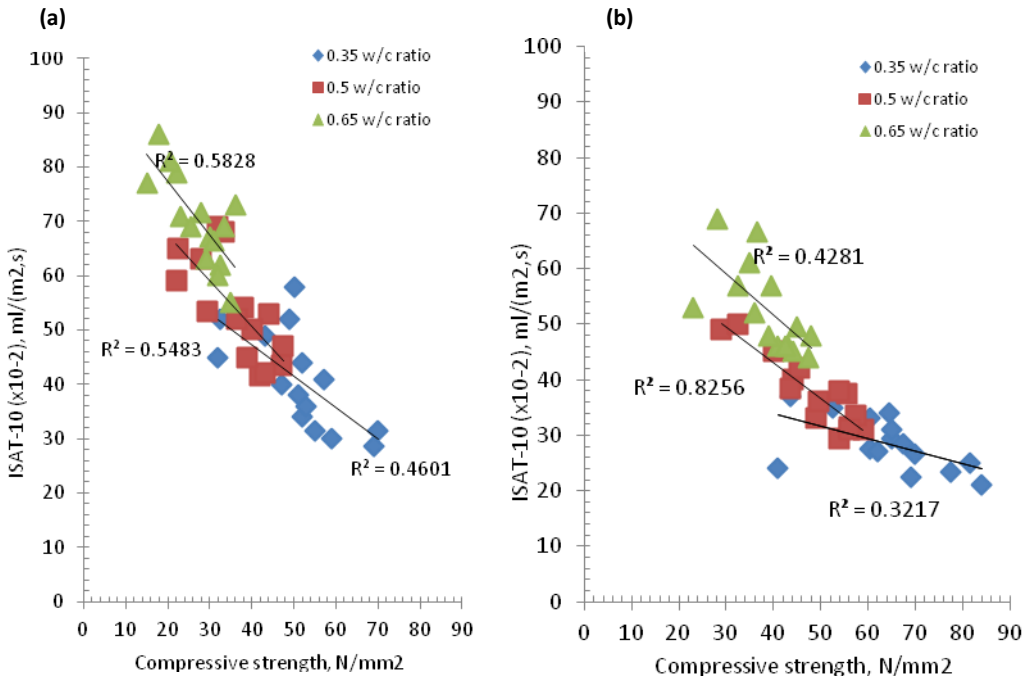


Fig: 6.14: ISAT v Compressive strength for (a) 28 days and (b) 180 days

For the sorptivity data the correlation is poor across all w/c ratios at both 28 and 180 day testing, with the results widely scattered (Figure 6.15). Such results would indicate that

there is no direct relationship between absorption and compressive strength and any result is dependent on the materials used, water content and curing.

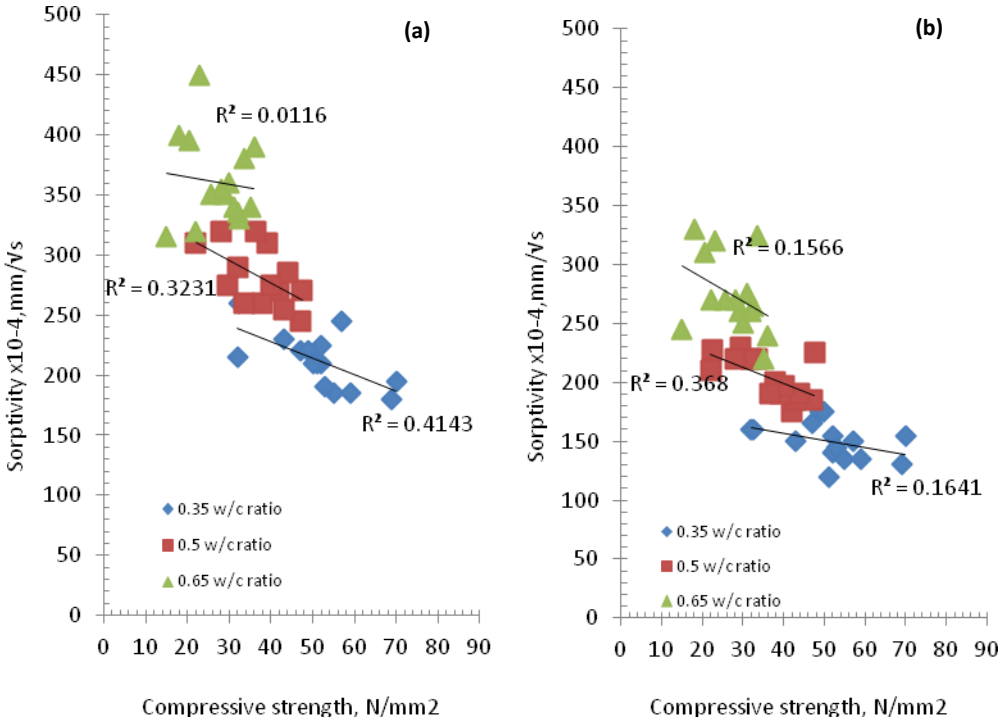


Fig 6.15: Sorptivity v Compressive strength for (a) 28 days and (b) 180 days

Similarly when viewed together, Figure 6.16, no correlation is seen between ISAT and sorptivity clearly indicating that whilst both provide a measure of absorption there must be inherent differences. Both tests, by their nature, test the absorption characteristics of the surface zone of concrete and not its core but this is where the similarities end. The preconditioning of the samples differ, as previously discussed, given that surface absorption is sensitive to moisture conditions this may be enough to cause differences within the results. Whilst it is relatively simple to achieve a constant weight by oven drying which will ensure the removal of moisture, air drying may be less reliable and yet the sorptivity test itself requires the sample to be only unsaturated with a small amount of moisture required for capillary suction to occur. In addition sorptivity is a measure of one dimensional capillary absorption as a fraction of time; depth of water penetration is measured indirectly through weight gain and the

sorptivity is calculated from the slope of the curve of the weight gain against time and converted into mm/s^{½}. With ISAT the geometry of the opening of the cap, together with its contact with the concrete creates a two dimensional absorption (*CCAA, 2009*). The flow of water in this test is also assumed to be unidirectional.

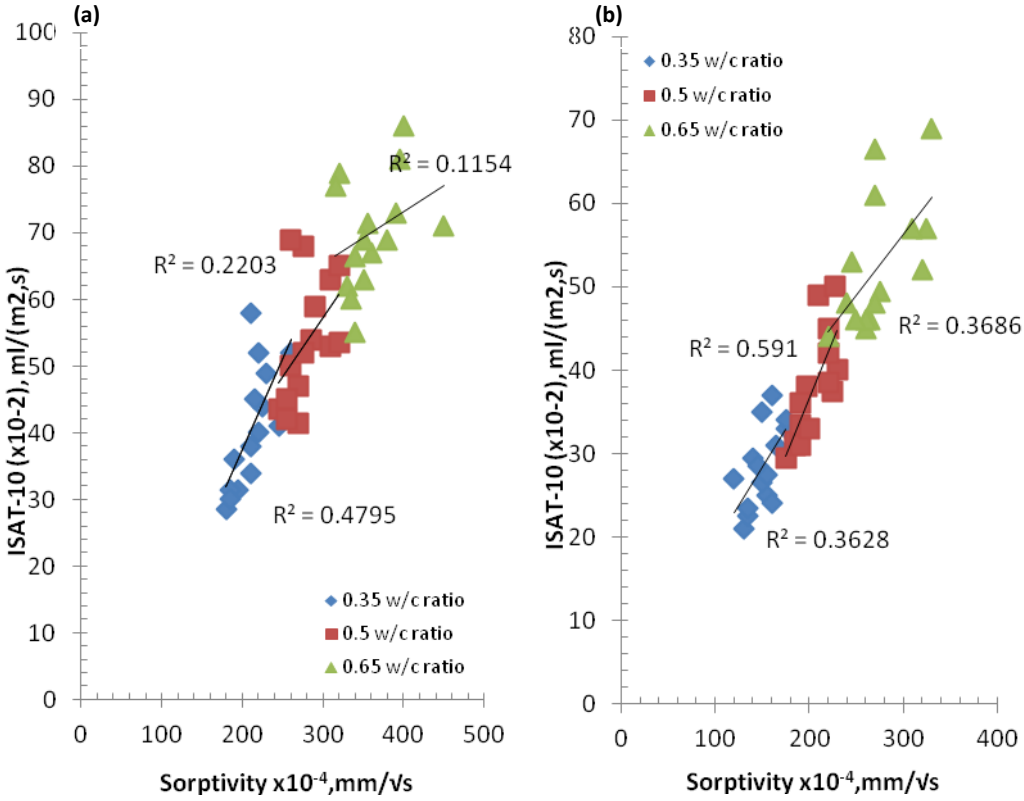


Fig 6.16: Sorptivity v ISAT for (a) 28 days and (b) 180 days

6.4.1 ISAT-10 for Equivalent Compressive Strength of 40 N/mm²

By interpolating the w/c ratios for equivalent strength of 40 N/mm^2 (as discussed in Chapter 5), it is possible to compare the surface absorption for the cement combinations on this basis. At the earlier test age (28 days) it is the limestone ternary mixes that gives lower absorption results, whilst the longer curing time allows the fly ash to react further and provide better results following 180 days curing. The greater improvement with curing time has generally been seen with the fly ash mixes, indicating that the prolonged curing time allows further pozzolanic activity of the materials. The limestone ternary concrete did show some improvement with time but it is likely that this is more due to the effects of prolonged curing

on the GGBS in the mix combinations, and not the filler effects of the limestone. Tasdemir (*2003*) stated that concretes with identical strengths may not provide the same permeation properties and this is clearly evident for the absorption properties shown in Figures 6.16 and 6.17. Whilst all mixes have a strength of 40 N/mm^2 at 28 days, both the initial absorption and the sorptivity vary depending on the cement combination and because the w/c ratio of each mix is different in order to attain the same strength at 28 days. With the water content fixed at 165 l/m^3 this meant, therefore, that the volume of cementitious materials differs to compensate for the different w/c ratios and is possibly a contributing factor due to the varying cement content. As noted in Chapter 5 (Figure 5.9) in the main the w/c ratios ranged between 0.4 and 0.58 for the combination concretes in order to achieve equivalent strength. The better ISAT values are attained at the lower w/c ratios, as already discussed. An increase in w/c ratio decreases the cement and additions with in the mix design, creating more voids within the structure. Across the range of ternaries this is not a significant issue as these concretes will still give average ISAT values.

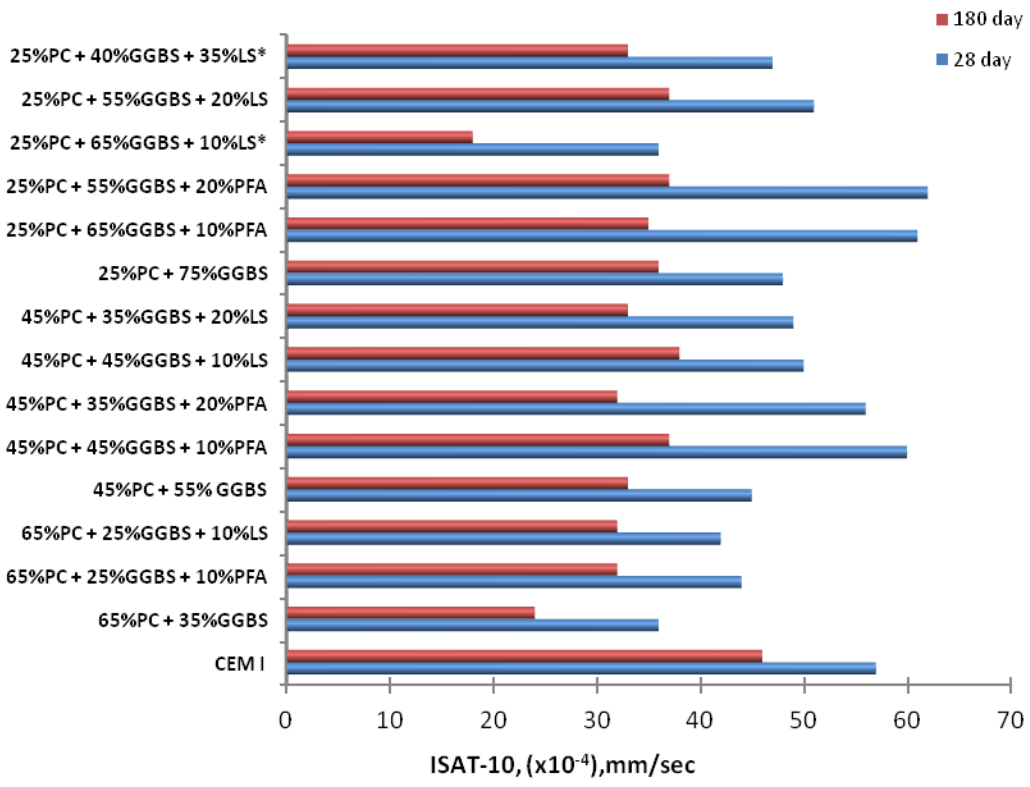


Fig 6.17: ISAT-10 for equivalent strength 40N/mm^2

6.4.2 Sorptivity at Equivalent Strength of 40 N/mm²

As with the previous ISAT results, the sorptivity data was also compared at an equal 28 day strength of 40 N/mm². The earlier discussion indicated that the 10% fly ash ternary concrete at the 35% addition level gave the better sorptivity results for the 0.5 and 0.65 w/c ratios by 180 days. To achieve equivalent 28 days strength of 40 N/mm² the w/c ratio would be required to be 0.53 and whilst at 28 days the sorptivity for this mix was high, by 180 days it was greatly improved.

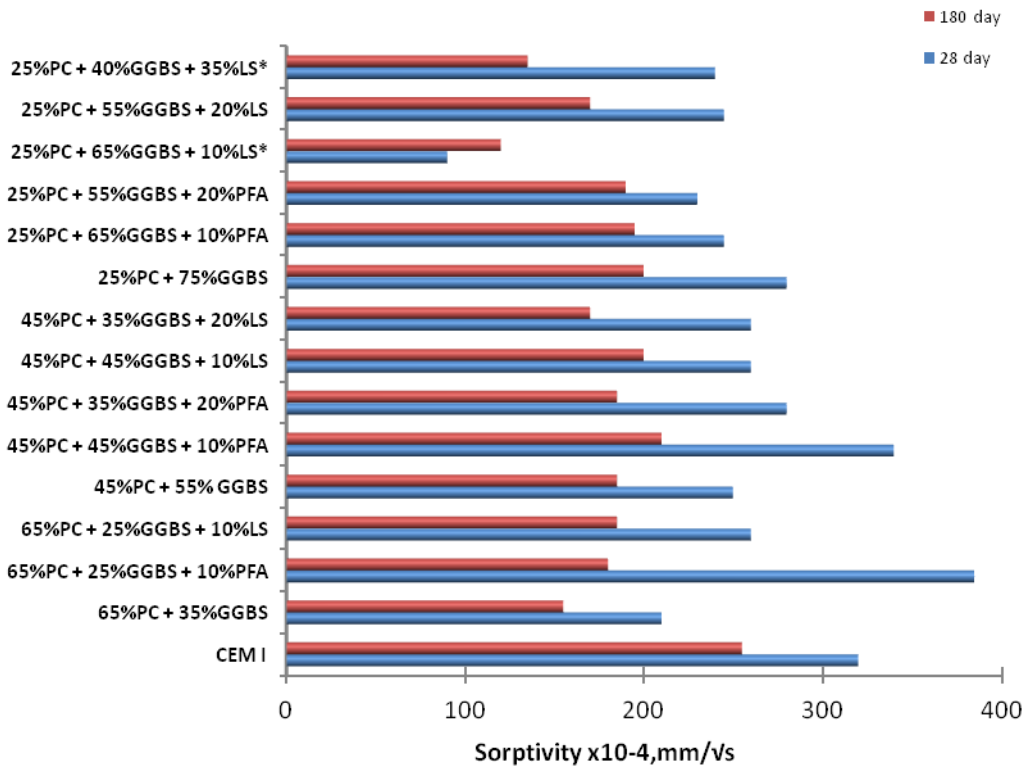


Fig 6.18: Sorptivity for equivalent strength 40N/mm²

6.5 Absorption v Porosity

It was previously stated that sorptivity, or sorption force, is inversely proportional to the diameter of the pores within the structure of concrete, with smaller pores causing higher sorptivity (*Kelham, 1988*). With this in mind it would be prudent to examine the porosity in relation to the absorption data for selected samples. The porosity of the concrete was

discussed briefly in the previous chapter with regard to its relationship to compressive strength; here it will be examined in more detail.

The pore system of concrete is not a constant and will be affected by curing time, moisture content and exposure conditions. The porosity of cement paste will therefore be dependent on the w/c ratio and age of the sample due to the effect of both on the gel/space ratio. As stated by Mills (*1986*) the actual porosity of the system is a function of the amount of water introduced at mixing with the hydration process determining the extent of the filling and also the redistribution of original pore spaces. Figure 6.19 illustrates the effect of the hydration products in filing pores within the cement paste matrix. Table 6.5 shows both the effective capillary porosity and the critical pore size, determined by MIP for selected cement pastes at 0.35 and 0.5 w/c ratios. Appendix C details the process of interpolating the results to obtain this data.

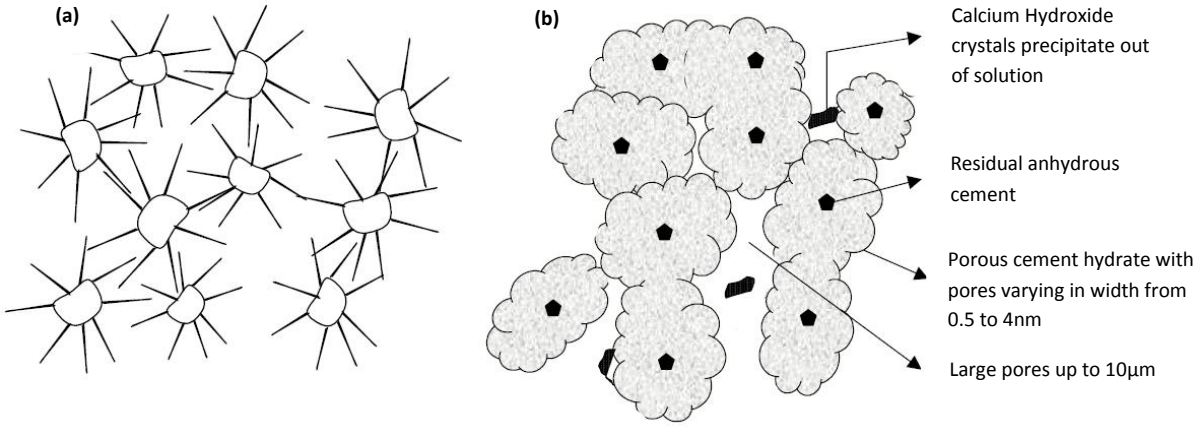


Fig 6.19: Pore filling by products of hydration

(a) Cement grains at time of final set; (b) fully hydrated cement paste (Mills, 1986)

Table 6.5: Total porosity and critical pore size for selected cement paste samples

Mix Combinations	28 day		180 day	
	Total Porosity (%)	Critical Pore (nm)	Total Porosity (%)	Critical Pore (nm)
0.35 w/c ratio				
CEM I	22	51	17.5	40
65%PC + 35%GGBS	20.5	45	15.5	36
65%PC + 25%GGBS + 10%PFA	20	50	16	40
65%PC + 25%GGBS + 10%LS	22	63	17.5	50
45%PC + 55% GGBS	21	55	16	40
45%PC + 45%GGBS + 10%PFA	20.5	65	16.5	45
45%PC + 45%GGBS + 10%LS	22	85	19	65
0.5 w/c ratio				
CEM I	24	120	21	100
65%PC + 35%GGBS	23	105	19.5	90
65%PC + 25%GGBS + 10%PFA	23	112	20.5	95
65%PC + 25%GGBS + 10%LS	23.5	120	20	105
45%PC + 55% GGBS	23	130	20.3	100
45%PC + 45%GGBS + 10%PFA	23	145	20.5	105
45%PC + 45%GGBS + 10%LS	24	150	21	125

It is suggested by Pipilikaki & Beazi-Katsioti (*2009*) that the critical pore size controls the transmissivity of the material, concurring with Aligizaki's earlier study (*2006*), with the critical pore diameter being that most frequently occurring in the interconnected pores, allowing maximum percolation of fluids through the cement pores. Pipilikaki & Beazi-Katsioti found that with a 35% addition of limestone, creating limestone cement, the critical pore size can double from 20nm to 40nm. This suggests that the filler effect of limestone at lower levels is not seen with the higher volume, the average particle size will have reduced, due to the greater volume of limestone creating a dilution effect, compared to the mixes containing less limestone.

When related to both ISAT and sorptivity values, it can be seen that the larger critical pore size gave greater absorption values. The 0.35 w/c ratio had lower values, decreasing with longer curing to 180 days. The higher w/c ratio increased the values as already discussed for ISAT and sorptivity, but also for the critical pore size. The 35% GGBS level mixes reduced the critical pore size compared to the CEM I for the 0.35 w/c ratio, an increase in GGBS level to 55% increased the critical pore size slightly and consequently the ISAT values. The inclusion of fly

ash had the effect of increasing the critical pore size compared to the binary at the 0.35 w/c ratio at both addition levels, with raised ISAT values. At 28 days, the critical pore size of the limestone ternaries at 35% GGBS level was high whilst the ISAT value was low, prolonged curing to 180 days gave more related results as seen in Figure 6.20(c).

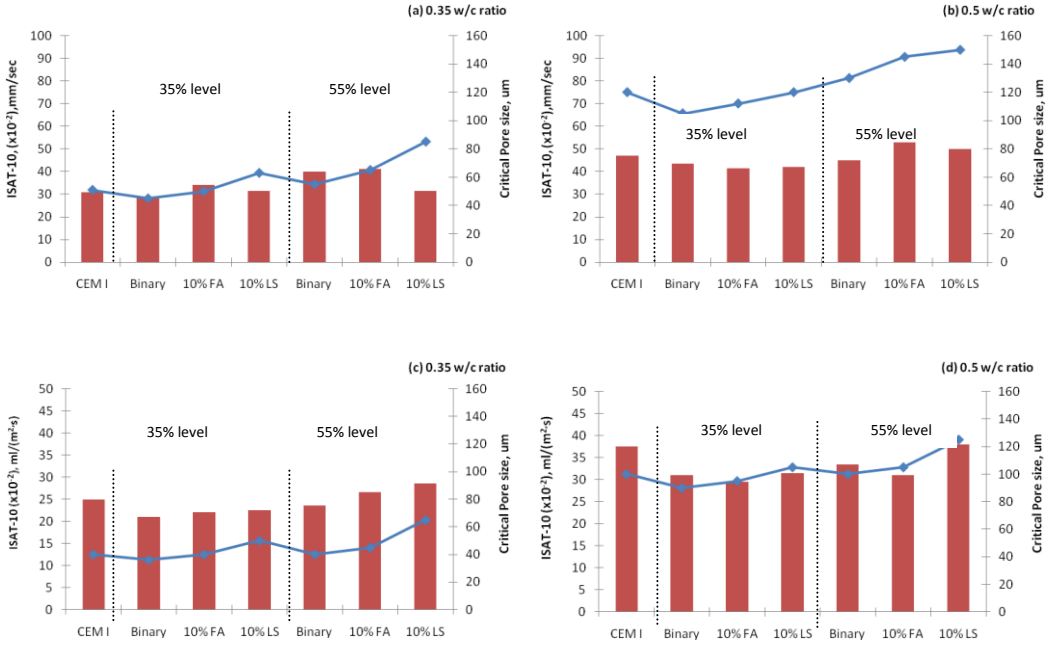


Fig 6.20: ISAT-10 against critical pore size at 28 days [(a) and (b)] and 180 days [(c) and (d)]

Tsivilis et al (*2003*) state from their findings that concrete with limestone generally has a lower porosity and a low mean pore size compared to CEM I. It was, however, clear from the data presented in Figures 6.20 and 6.21 that this did not apply to the current study. Whilst there is agreement concerning the increased sorptivity with limestone level; it is possible that this difference is due more to the process and production of the cement and physical properties and quality of the limestone used. Tsivilis et al (*2003*) co-ground limestone, clinker and gypsum to produce limestone cements. In this study the limestone was added during mixing and therefore its structure may have been very different to that of Tsivilis et al(*2003*). It

is also apparent that when mixed with GGBS to form a ternary concrete the effect of the limestone reported by Tsivilis et al (*2003*) was not as obvious as it had been when diluted by GGBS.

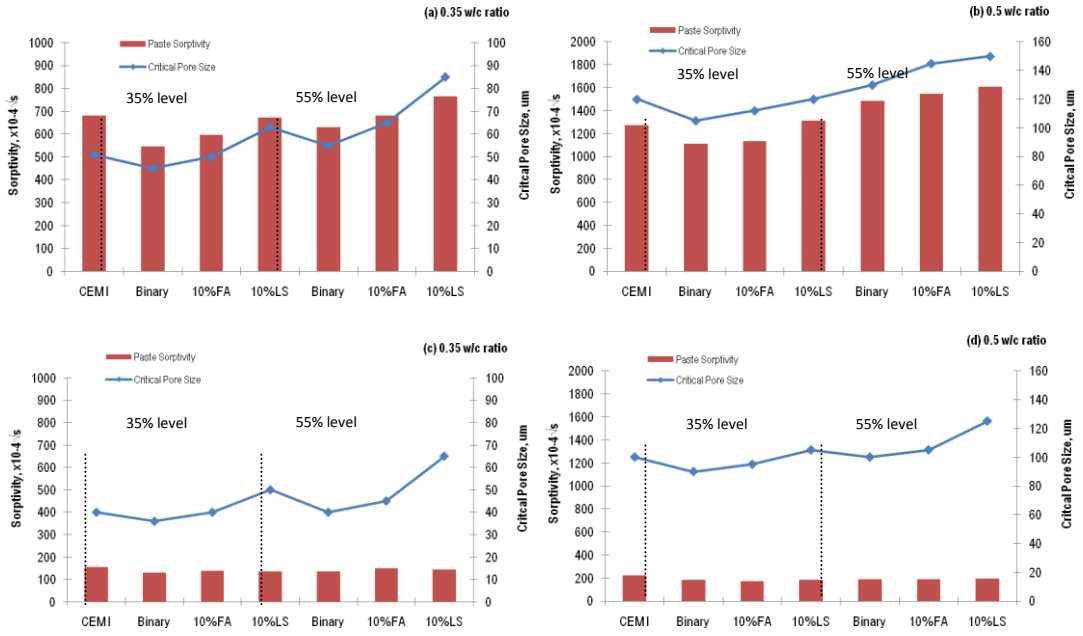


Fig 6.21: Sorptivity against critical pore size at 28 days [(a) and (b)] and 180 days [(c) and (d)]

To examine Kelham's theory the pore diameter is plotted against the sorptivity both collectively (Figure 6.22) and for independent addition levels (Figure 6.23). It was clear from this that that was not an inverse relationship between the porosity and sorptivity but the opposite. The majority of pores measured at both w/c ratios and at both test ages fell within the medium and large capillary classification according to Mindess (*2003*) (refer to Table 6.1) although the range of their sizes was quite wide, from 36nm to 150nm. All that can be agreed upon is that both critical pore size and porosity reduce with both w/c ratio and time but this was not unexpected.

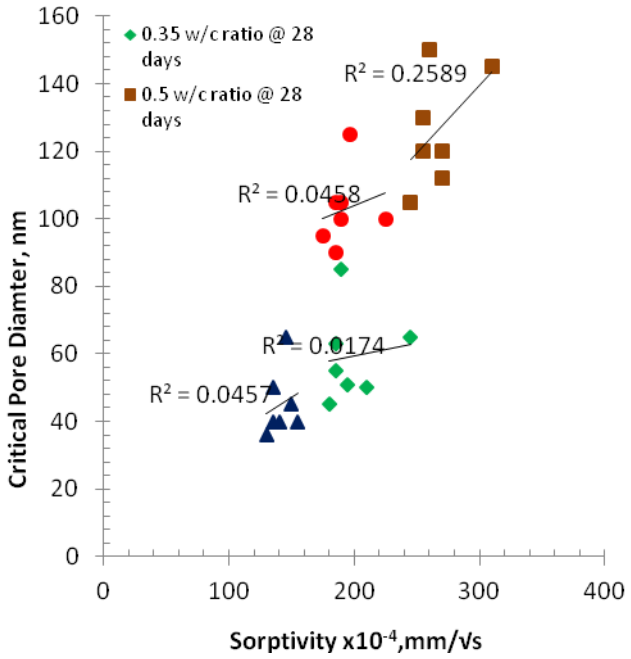


Fig 6.22: Sorptivity v Critical PoreDiameter by w/c ratio and test age

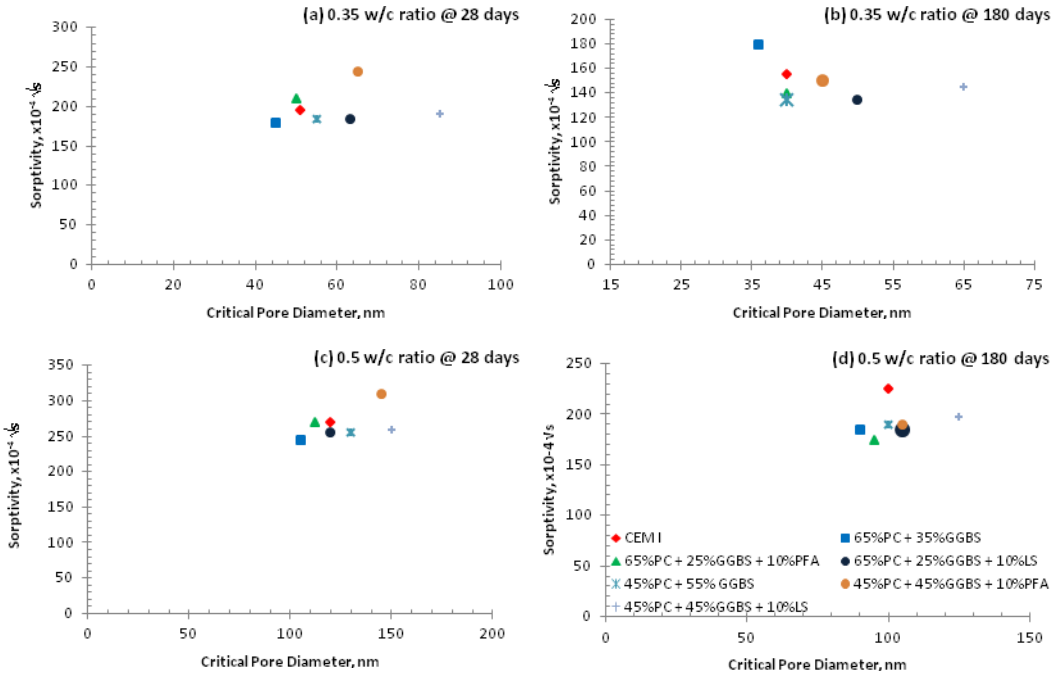


Fig 6.23: Sorptivity v Critical pore diameter by mix combination, w/c ratio and test age

Little correlation also exists between the critical pore diameter and total porosity for any cement paste other than the 0.35 w/c ratio at 180 days as shown in Figure 6.24. Clearly an increase in critical pore size is not indicative of an increase in porosity. It would seem that there are additional factors that need to be taken into consideration that may influence the results of the MIP tests. Not only is there the obvious difference between the concrete specimens used in the absorption tests and the cement paste samples used for the MIP in that the former contains aggregate, but both sample conditions and the rate of pressure can affect the results as can a maximum intrusion pressure and surface tension of mercury (*Kumar & Bhattacharjee, 2004*).

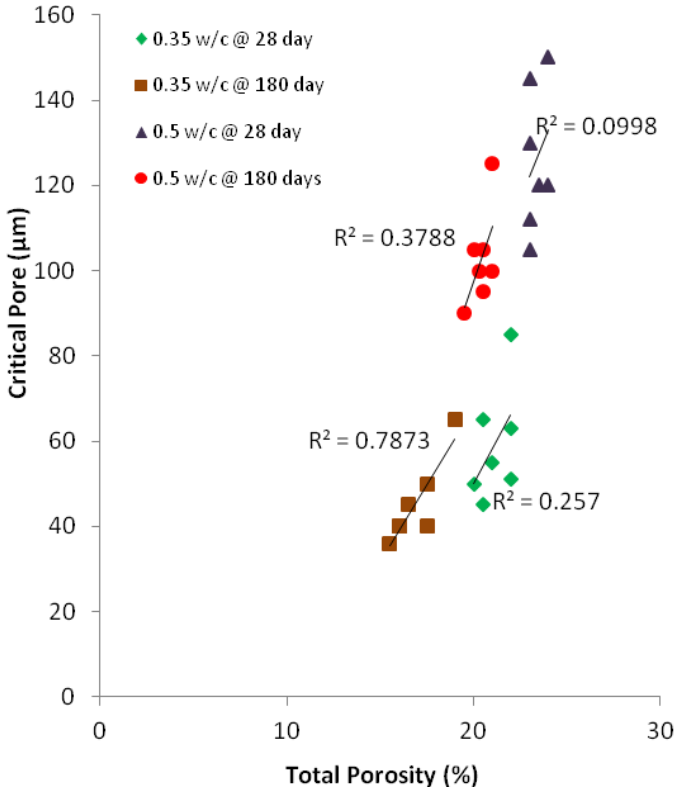


Fig 6.24: Porosity v critical pore diameter by w/c ratio and test age

For the test to be successful the mercury has to pass through the narrow pores connecting the pore network (*Cook & Hover, 1999*). If the pores are too small or isolated, the mercury may not intrude although it is possible that the pressure applied during the test can cause a collapse of the thinner pore walls, breaking through to isolated ones. The size of the

pores influencing the results may also differ and, in addition, an “ink bottle” effect can occur due to the pressure applied to the mercury so that narrow pore openings may widen into larger pores. Whereas water during the absorption tests has little or no force applied to it. These pores may not be affected in the same way as with MIP where the pressure applied can force the mercury into these voids.

6.6 Sorptivity of Cement Paste in Relation to Concrete

Given the lack of relationship between the results it may be concluded that the role of the ITZ is more far reaching than originally considered, this maybe considered in conjunction with the porosity of the aggregates within the concrete matrix itself, however, the aggregates used in this study had low absorption properties. It has already been postulated that the former is the most porous and indeed weakest, giving the least resistance to liquids or gases. The aggreagtes themselves were tested and found to be of low porosity, their addition to the mix would therefore only increase tortuosity and thus reduce sorptivity when compared to that of cement paste. The sorptivity of selected cement paste samples was tested at 28 days to allow for comparison between them and their concrete counterparts. When the sorptivity data for paste and concrete is plotted against each other there appears to be no correlation as shown in Figure 6.25, with the sorptivity of paste showing a greater range of results.

However, when examining each mix individually by w/c ratio, comparison can be seen. From the data the sorptivity ratio (S_r) of concrete (S_{con}) to paste (S_{paste}) was calculated using the following formula and the results are given in Table 6.5.

$$S_r = \frac{S_{con}}{S_{paste}}$$

[Eq 6.1]

Comparisons are more clearly observed in Figure 6.26 where the sorptivity ratio of concrete to cement paste does not differ greatly between w/c ratios, with the 0.35 w/c ratio marginally increased compared to the 0.5. It can be concluded from this that the effect of adding aggregates to form the ITZ has similar consequences for both w/c ratios. The continuity of the pore system may differ between the w/c ratio. The increased volume of cement paste to fixed

mix water for the lower w/c ratio will also mean reduced sorptivity due to the reduction in water content. For the 0.5 w/c ratio the volume of aggregates in the mix has increased (refer to Table 3.4). This will have the effect of increasing the toruosity, cancelling out the effect of the lower volume of cement paste and increased mix water. Generally it was seen that the ratio also reduced slightly with an increasing level of GGBS replacement for the binary mixes. The 10% addition of fly ash, forming ternary mixes, increases the ratio whilst the addition of 10% limestone reduced the sorptivity ratio with increasing replacement level.

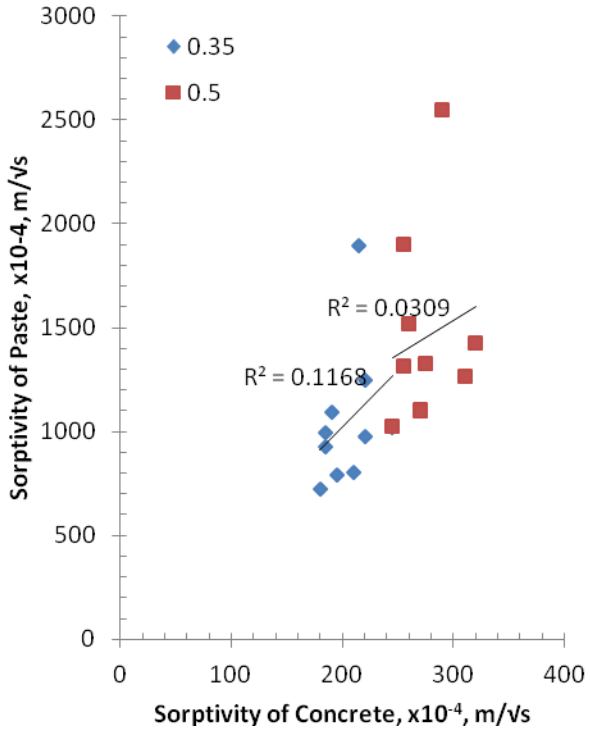


Fig 6.25: Sorptivity of paste against concrete for selected samples at both w/c ratios

Table 6.5: Sorptivity of selected paste and concrete with concrete to paste ratio at 28 days

Mix Combination	Paste	Concrete	S_r
0.35 w/c ratio			
CEM I	791	195	0.25
65%PC + 35%GGBS	725	180	0.25
65%PC + 25%GGBS + 10%FA	805	210	0.26
65%PC + 25%GGBS + 10%LS	925	185	0.20
45%PC + 55% GGBS	993	185	0.19
45%PC + 45%GGBS + 10%FA	975	245	0.25
45%PC + 45%GGBS + 10%LS	1095	190	0.17
25%PC + 75%GGBS	1250	220	0.18
25%PC + 65%GGBS + 10%FA	1020	220	0.22
25%PC + 65%GGBS + 10%LS	1897	215	0.11
0.5 w/c ratio			
CEM I	1103	270	0.24
65%PC + 35%GGBS	1028	245	0.24
65%PC + 25%GGBS + 10%FA	1098	270	0.25
65%PC + 25%GGBS + 10%LS	1315	255	0.19
45%PC + 55% GGBS	1427	255	0.18
45%PC + 45%GGBS + 10%FA	1269	310	0.24
45%PC + 45%GGBS + 10%LS	1521	260	0.17
25%PC + 75%GGBS	1900	320	0.17
25%PC + 65%GGBS + 10%FA	1327	275	0.21
25%PC + 65%GGBS + 10%LS	2547	290	0.11

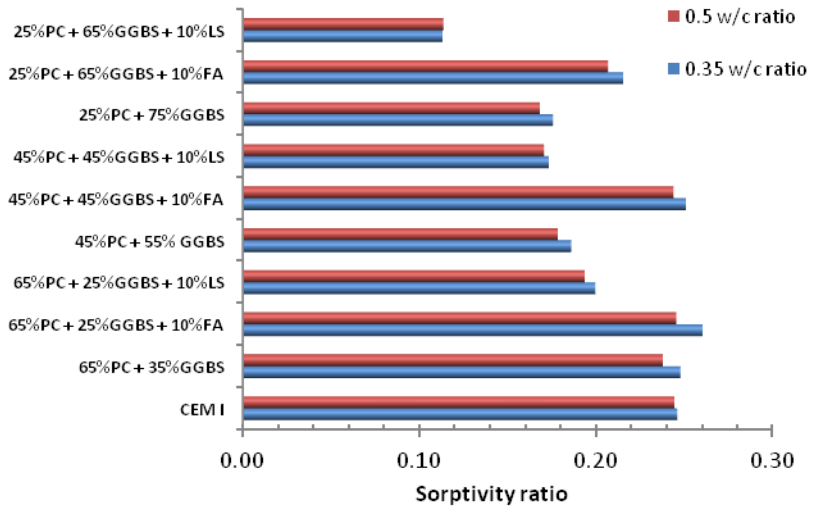


Fig 6.26: Sorptivity ratio for selected mix combinations tested at 28 days

6.7 Summary

In this chapter, the effects of addition materials have been discussed in relation to the absorption properties of concrete. The importance of concrete being able to limit the absorption of fluids to which it is exposed during its service life, in order to maintain a durable concrete.

Overall it was evident that an increase in w/c ratio had the effect of increasing both the ISAT and sorptivity of the mix combinations. Extended curing to 180 days reduced the ISAT and sorptivity values as supported by the literature and discussed within this chapter; these results were as expected.

The binary mixes at the 35% and 55% addition levels gave reduced ISAT and sorptivity values across the range of w/c ratios, when compared to the CEM I control concrete, which was further improved by prolonged curing to 180 days. The GGBS produced a denser microstructure with more pore space filled with C-S-H. The 75% level gave poorer results overall at 28 days but were improved at the higher w/c ratio.

The addition of fly ash to produce ternary concretes had differing effects across the range of GGBS levels and w/c ratios. At the 35% replacement level and lower, 0.35, w/c ratio the fly ash offered no improvement on the binary mix. With 25% GGBS and 10% fly ash competition occurs between them both for hydroxyl ions being produced by the CEMI/ water reaction, slowing the reaction of both the GGBS and fly ash and also the production of a denser microstructure. An increase in w/c ratio at this replacement level improves the rate of reaction improving absorption values.

An increase in replacement level to 55% gave increased ISAT values for the 10% fly ash across the range of w/c ratios at 28 days. Prolonged curing improved the absorption of the 10% fly ash, allowing continued hydration to take place, creating a denser microstructure, making it more comparable with the binary mixes. The sorptivity followed a similar trend but the improvement of prolonged curing was more noticeable. Little difference was seen with an increase to 20% fly ash for ISAT values at the 0.35 and 0.5 w/c ratios, but it was clear that the

w/c ratio does have an effect on the reaction of these ternary mixes with improvements seen with an increase to 0.65 w/c ratio. For the sorptivity tests, the 20% fly ash reduced the value at 28 days compared to the 10% fly ash ternary which is likely to be due to its ability to compete effectively with GGBS for the lime. However, the prolonged curing shows an increase compared to the 10% fly ash. The 75% addition, overall, indicated an increase in absorption values for the fly ash ternary mixes for ISAT. The sorptivity again gave contrary results showing improvements for both ternary mixes at 28 days and after 180 days curing.

The limestone ternary mixes at the 35% addition level gave comparable results with the binary mix across the range of w/c ratios and test ages for both ISAT and sorptivity values. At the 45% addition level an increase to 20% limestone gave better ISAT values following prolonged curing compared to 10% limestone that was better at the earlier, 28 day, test age, making it comparable with the binary mix. This was also reflected in the sorptivity results. In general, with an increase in level to 75%, the 10% limestone was better than both the 20% and 35% limestone additions, which was also reflected by the sorptivity values. By 180 days, at the 0.35 w/c ratio, it is comparable to the CEM I and at 0.65 w/c ratio it is comparable with the binary mix and improved on the CEM I mix.

The critical pore size was generally shown to increase with absorption indicating a strong correlation between the two for both 0.35 and 0.5 w/c ratio. It was, however, found that the limestone ternary mixes had an increased critical pore size which has been previously reported by Tsivilis et al (*1999*) that a 10% limestone cement had the ability to reduce the critical pore size. This indicates the additional effects of processing, quality of material and mix combination. Further, Kelham's observation of an inverse relationship between critical pore diameter and sorptivity was not proven with the opposite effect occurring, in addition no correlation was observed between the critical pore size and porosity. When compared together, selected paste samples and their concrete counterparts were used to calculate a sorptivity ratio, the ratio across both w/c ratios ranged from 0.11 to 0.26 with little difference between w/c ratios for each individual mix combination examined indicating similar reactions within the concrete matrix with the addition of aggregates creating an ITZ.

CHAPTER SEVEN: AIR PERMEABILITY & WATER PENETRATION

7.1 Introduction

In addition to the absorption of concrete discussed in Chapter 6, permeability of cement combination concretes was measured using air and water as the test fluid. The permeability of concrete is relevant where it is to be used in a water retaining or similar structure (*Concrete Society, 2008*). The transportation of air and water can contribute to the deterioration of concrete and are related to processes including chloride ingress, carbonation and freeze/thaw damage. The former two will both be discussed in the following chapter. As a rule, depending on both the ambient conditions and the thickness of the concrete itself, most of the capillary water and part of the absorbed water evaporates leaving the pores empty or unsaturated (*Mehta & Montiero, 2004*). It is the evaporable water that is free for internal movement within the concrete matrix. If the hydraulic conductivity, referred to more commonly as the coefficient of permeability (*k*), is low then the concretes vulnerability to any water related destructive phenomena will be limited so long as there is little, or indeed, no water remaining in the matrix after drying and it is not exposed subsequently to an environment that may cause re-saturation of the pore system. Permeability is the property of concrete that governs the rate of flow of a fluid into its porous structure under a pressure head. It is a global coefficient (*k*) that is determined by Darcy's Law:

$$\frac{dq}{dt} = k\,\frac{\Delta H A}{L\mu}$$

[Eq 7.1]

Where dq/dt = rate of fluid flow

μ = viscosity of fluid flow

ΔH = pressure gradient

A = surface area

L = thickness of solid

Both air permeability and water penetration under pressure tests were carried out in order to obtain further information about the microstructure and durability properties of the test concretes. The intrinsic permeability (hence forth simply referred to as permeability) of gases and water vapour is said by Mehta & Montiero to be lower than that for liquid water, with tests generally carried out using water that has no dissolved air to avoid any difficulties in interpreting the results. In the absorption tests, water was applied under a 200mm head (low pressure to dry concrete) and this was drawn in by capillary suction. In many cases, the smaller pores do not affect the transport of fluids until pressure is applied, forcing their entry. Again preconditioning of the test specimens is of importance in relation to these types of measurements. Indeed, air permeability test specimens needed more preparation, with a core required to be cut from a 100mm cube sample, compared to the water penetration test, which was carried out on a 150mm cube specimen that required no preconditioning other than water curing for until the specified test ages. The specimens were removed from the curing tank and placed directly in the test rigs at the set test ages (28 and 180 days). The cored samples for air permeability tests were oven dried to constant weight. In spite of this, it may be possible that such preconditioning may affect the permeability by the possible creation of gradients of moisture through the concrete in turn causing micro-structural modifications (*Elahi et al, 2010*). However, forced drying in this way is considered to minimise, if not remove this effect (*Ramachandran & Beaudoin, 2001*). In addition to the moisture content, other factors may also affect the permeability of concrete. The ambient conditions at the time of tests have previously been highlighted in earlier chapters where it was noted that all test conditions were standardised in order to prevent the effects of temperature on the viscosity and surface tension of fluids and humidity effects on the flow mechanism.

The driving force and duration of the test may also affect permeability. The air permeability test itself is quick and non-destructive allowing a number of pressures (as described in Chapter 3) to be tested on one specimen with relative ease. The method for carrying out the water penetration test requires the specimen be clamped into the testing rig for 72 hours and then split. Ramachandran & Beaudoin (*2001*) suggest that this length of

testing may cause further changes in the permeability. As well as causing further hydration, impurities in the water may cause silting and a chemical reaction in the concrete. It is also possible that calcium hydroxide washed onto the bottom surface of the test specimen may carbonate (due to the atmosphere) forming an impermeable layer. The test methods were followed stringently in order to avoid any such effects on the permeability of the concrete test specimens. However, some effects, such as carbonation and hydration are out with any control and will occur due to the nature of the tests, preconditioning and curing. All combinations across the range of w/c ratios were tested.

7.2 Intrinsic Air Permeability

Air permeability tests were carried out in accordance with the test method described in Chapter 3. After oven drying to a constant weight, cored samples measuring 54mm diameter and 50mm length were placed in the apparatus and tested at a range of pressures, from which the intrinsic air permeability was determined. As with previous tests, a CEM I control mix was used to provide a comparison. Figures 7.1, 7.3 and 7.4 show the intrinsic air permeability results recorded for all combinations across the range of w/c ratios. The intrinsic air permeability of the binary and ternary mixes are shown relative to that of the CEM I concretes in Figure 7.5.

7.2.1 35% GGBS Level

At 28 days, the air permeability results off the CEM I and binary concretes were comparable at 0.35 w/c ratio, as shown in Figure 7.1. This increased with the addition of 10% fly ash in the ternary concrete, whilst 20% limestone gave comparable results to both CEM I and binary concretes. An increase in w/c ratio to 0.5, increased the air permeability of the concretes, which increased further as this was raised to 0.65 w/c ratio. Across this range of w/c ratios at 28 days, the 10% fly ash ternary also gave progressively higher results, with increasing w/c ratio. The 10% limestone ternary concrete, however, gave the better results across the range of mixes at the various w/c ratios, with little difference seen between the 0.35 and 0.5 w/c ratios for this mix. This was significantly lower than the CEM I, binary and 10% fly ash ternary concretes at the higher w/c ratio. By 180 days, the air permeability was lower across the range of cement combinations and w/c ratios. The greatest improvements were seen with

the binary and ternary concretes at 0.5 and 0.65 w/c ratios, with the 10% limestone still lowest. The CEM I concrete did not significantly improve with prolonged curing to 180 days.

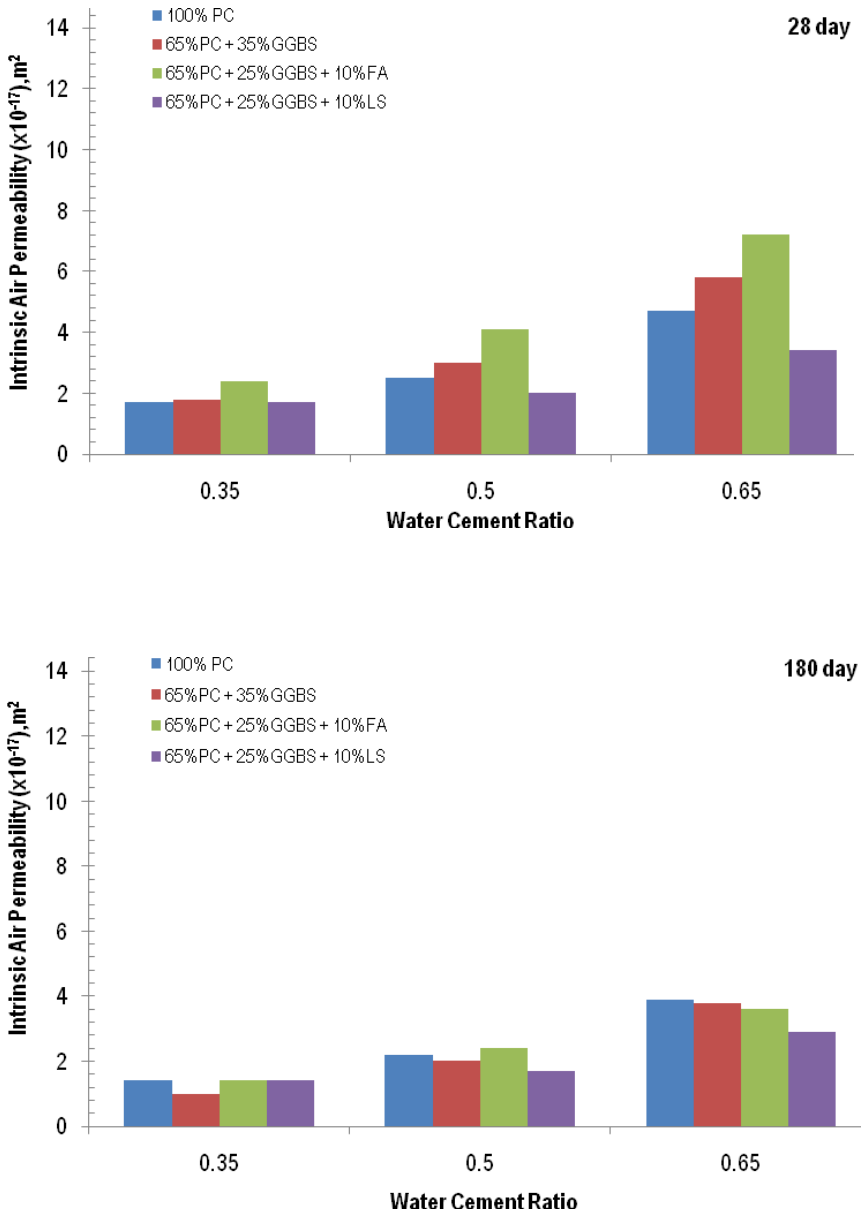


Fig 7.1: Intrinsic Air Permeability of 35% GGBS level concretes

At the 35% GGBS level, the effect of limestone, when added to the binary concrete was evident. The limestone does not show pozzolanic properties and therefore the production of C-S-H will be limited (*Ramezanianpour et al, 2009*). It is, therefore, likely that the limestone acts mainly as an inert filler and by this means contributes to reducing pore space within the microstructure of concrete, as noted previously. Ramachandran & Zhay (*1986*) state that the addition of $CaCO_3$ from limestone acts as nucleation sites, thus accelerating hydration of cement. An earlier study by Ramachandran (*1984*) found that limestone becomes incorporated into the C-S-H phase affecting the structure of hydrated cement paste. These combined effects, as filler and host of nucleation site, may account for the lower values of the 10% limestone ternary concrete at this level.

By examining the calculated voids ratio for the test materials, based on the mix design and material properties, at this GGBS level, shown in Figure 7.2 for air permeability, it is clear that the lower voids ratio of the limestone ternary may have contributed to the reduction in air permeability observed. That there is little difference between 28 and 180 day results for the limestone ternary at the 35% level suggest little limestone reactivity and the limited changes occurring are due to CEM I and GGBS. A greater reduction is seen with the other ternary material, fly ash, suggesting that this together with GGBS is more reactive than the limestone ternary concrete as previously indicated. Due to the properties of the additional materials both the binary and fly ash ternary concretes were slower to react compared to the CEM I and 10% limestone concretes.

7.2.2 55% GGBS Level

An increase in GGBS level gave higher intrinsic air permeability compared to the 35% level, across the range of w/c ratios and mix combinations. The CEM I control mix gave lower results across the range of w/c ratios, with the 10% limestone ternary mix providing the best results compared to both the binary and other ternary concretes tested. The highest permeability at 28 days was noted in the fly ash ternary mixes, which increased further with w/c ratio. The increase in permeability with increasing w/c ratio was expected for all combinations and is similar to effects noted by Sanjuan et al (*1996*) and more recently by Elahi

et al (*2010*). The increase in binary and fly ash ternary concretes was more noticeable, as shown in Figure 7.3 (a) at 28 days.

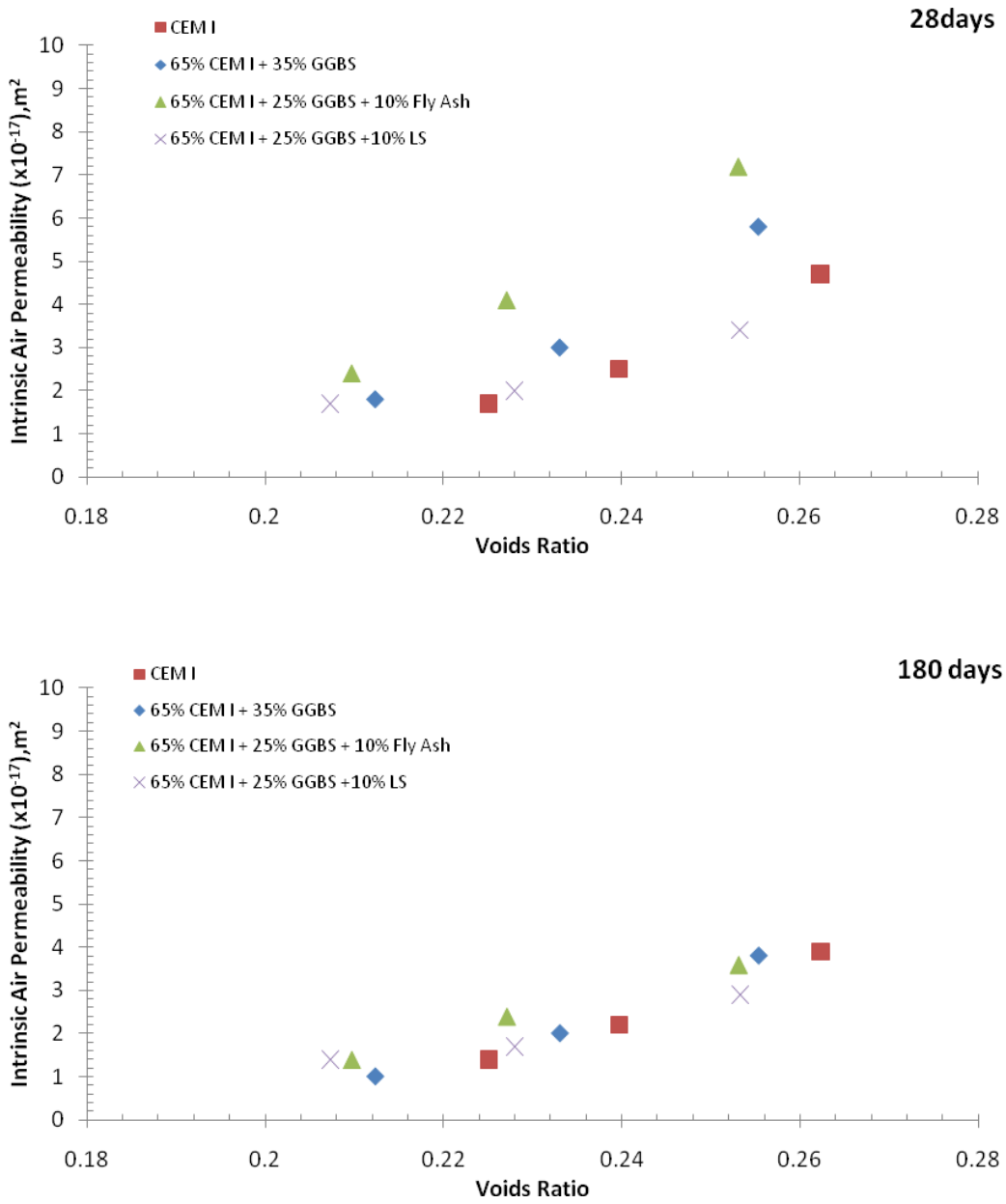


Fig 7.2: Intrinsic Air Permeability of 35% GGBS level concretes against void ratio of mixes

By 180 days, permeability reduced across the range of combinations and w/c ratios but CEM I remained lowest. The difference between fly ash and other concretes was reduced and at 0.65 w/c ratio the intrinsic air permeability was lower than that of the binary concrete, yet it was the 10% limestone ternary concrete mix that proved to be the best of the binary and ternary concretes at 0.5 and 0.65 w/c ratio. At 0.35 w/c ratio the binary was slightly improved and marginally lower than the 10% limestone ternary mix.

Whilst the CEM I concrete gave lower results, the effect of the limestone in reducing the permeability of the combination mixes was again apparent. The 10% limestone addition was more effective, acting as a filler, than at 20% where there was a diluting effect. That none of the combination mixes were comparable with those of the CEM I, suggests a diluting effect of the additional materials. An increase in GGBS level means a reduction in the volume of CEM I and consequently a diluting effect occurs (*Ramezanianpour et al, 2009; Bonavetti et al, 2003*) causing changes in the capillary porosity.

Pipilikaki (*2009*) studied the effect of limestone additions on the capillary pore size of concrete and found that an increase from 10% to 30% in a limestone binary altered the pore structure and doubled the size of the capillary pores. Tsivilis et al (2002) found that up to 15% limestone improved permeability and porosity, and above this level no effect was seen. Certainly, with the results shown in Figure 7.3, this is the case with the 10% limestone showing better results than at 20%, and better than GGBS binary concretes on the whole. It is the CEM I control mix, however, that was found to be least permeable.

Elahi et al (*2010*) tested a binary mix at 50% GGBS at 44 and 91 days which showed higher air permeability indices than the CEM I control mix at both test ages, supporting the results of this study. A binary of 20% fly ash showed improved air permeability at 44 days testing but increased at 91 days. This effect was not apparent when fly ash was added to the GGBS binary in this study, as indicated in Figure 7.3. Whilst as a binary material fly ash may have improved the air permeability as noted above at least when compared to GGBS binary concretes, it gave higher permeability as a ternary addition. It would seem that the effects of the fly ash are balanced by those of the GGBS, which is present in the greater proportions. This is likely to be

caused by competition for the lime produced by CEM I hydration with the GGBS, an increase from 10% to 20% fly ash may increase the competition thus increasing permeability due to a lower level of reaction.

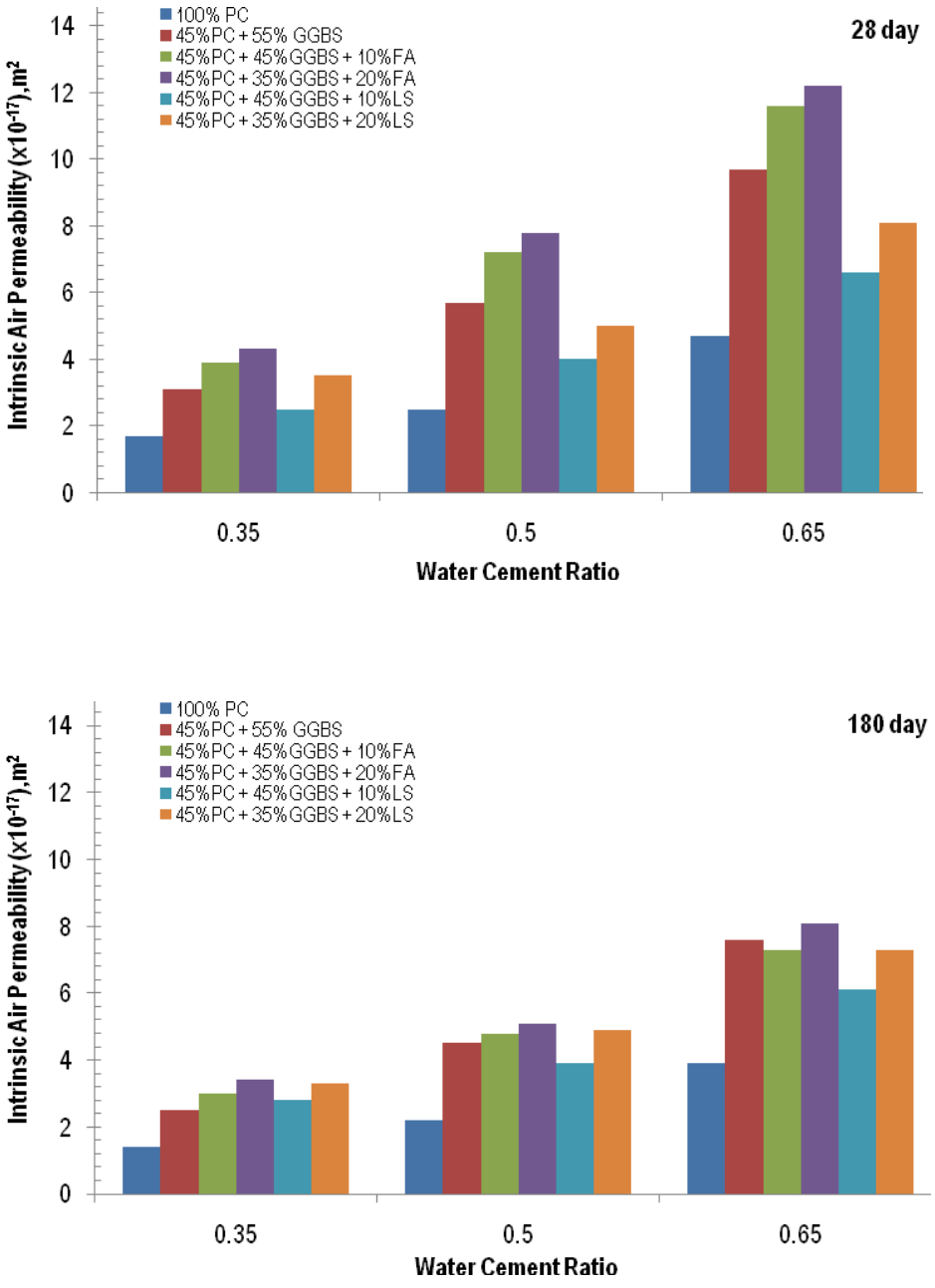


Fig 7.3: Intrinsic Air Permeability of concretes at the 55% GGBS level

7.2.3 75% GGBS Level

At this level, with an increase in GGBS content, the intrinsic air permeability increased further compared to the previous GGBS levels, yet still followed a similar trend to the previous levels of additions, as shown in Figure 7.4. The difference between CEM I and binary and ternary concretes was much greater with the CEM I giving the lowest results. At 0.35 w/c ratio, the binary mix was only slightly lower than the 20% limestone ternary, which was the lowest of the blended concretes at both 0.5 and 0.65 w/c ratios.

By 180 days, the binary and ternary mixes had decreased air permeability but this was much higher than CEM I concrete across the range of w/c ratios. The binary mix remained the lowest of the blended mixes at both 0.35 and 0.5 w/c ratio. At the 0.65 w/c ratio, both fly ash ternaries and the 20% limestone concrete were slightly lower than binary. The 70% GGBS binary mix tested by Elahi et al (*2010*) at 44 days was also much higher than the control mix, although a considerable improvement was seen in the binary mix by 91 days, due to the delayed reaction of the GGBS.

It is possible, as discussed by Aligizaki (*2005*) that permeation is not solely due to the pores found within the cement paste. Pores can also be found within the aggregates and the interfacial transition zone (ITZ) between this and the cement paste. The aggregates used in this study were of low porosity, as discussed in Chapter 3, and likely not to have a significant influence on the permeability (*Dhir et al, 2006*). Indeed Mehta & Montiero (204) state that when aggregate with a low permeability is combined with cement paste of high permeability, usually due to a high w/c ratio, it is expected to reduce the permeability of the concrete matrix overall due to increased tortuosity as the aggregate particles intercept the channels of flow within the cement paste. However, whilst it is stated that this is expected, rarely does it actually occur, indicating then that other factors are the cause. The microstructure of the ITZ is the most porous and weakest and may therefore be affected by the pressure applied during the test. Given the higher 75% level of GGBS, it is possible that this caused the higher permeability at 28 days and 180 days. The diluting influence of the binary and ternary material in the cement paste was unable to react and create bonds with the aggregates causing a weaker and more porous microstructure and large pores within the ITZ. The effects of

aggregates was also discussed by Elahi et al (*2010*) with regard to coarse aggregate in the mix affecting the size and volume of the ITZ, as well as the tortuosity of the flow path of the fluid or gas.

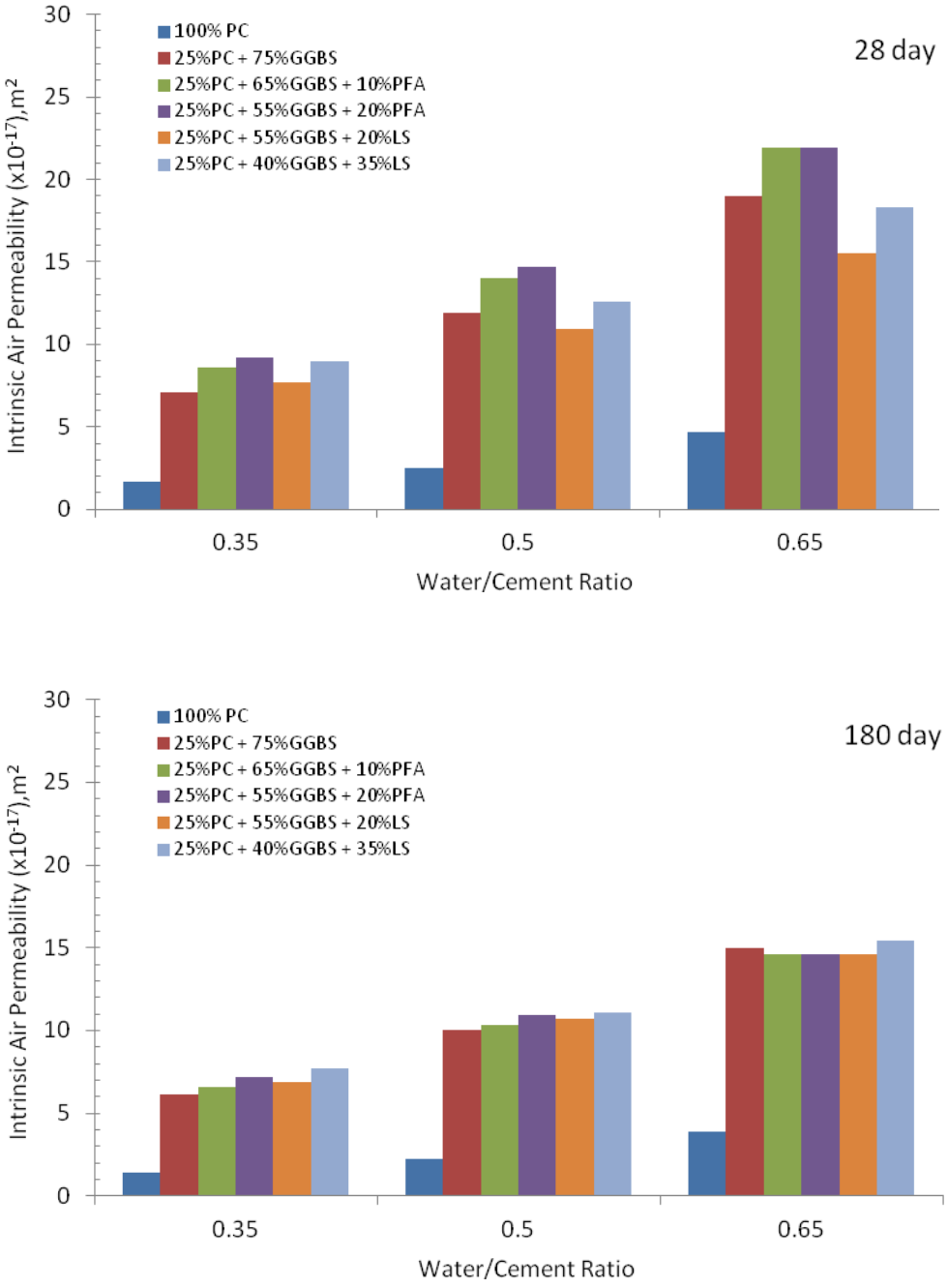


Fig 7.4: Intrinsic Air Permeability of 75% GGBS level concretes

The ITZ between the aggregate and the cement paste is stated by Basheer et al (*2005*) as being significantly different from the bulk cement paste with regards to both composition and density, as well as morphology. More importantly its porosity is higher (*Scrivener, 1996; Basheer et al, 2005*) thus having a significant effect on the permeability of concrete. Basheer et al (*2005*) found that a lower average size of aggregate within the mix can improve air permeability; indeed by increasing the fine aggregate content the air permeability decreased. Basher et al (*2005*) tested specimen mixes with 10mm and 20mm maximum coarse aggregate size. The aggregates used for the concrete mixes in this study were also graded into 4/10 and 10/20, as given in BS EN12620.

Humidity and temperature may also affect the cement structure (*Aligizaki, 2005*) but given the procedure that was followed for the preconditioning of each specimen it is unlikely that this would have been a factor in the current study. (A high paste content may cause more micro-cracking during drying in some cements than others.) Whilst there is little in the way of previous studies covering the specific ternary mixes considered here, similarities can be seen with the binary mixes examined in earlier papers. Alexander & Magee (1999) studied binary mixes of GGBS and silica fume in addition to combining them to produce ternary mixes. Elahi et al (*2010*) also studied the air permeability of GGBS and silica fume ternary concretes. Contrary to Alexander & Magee's findings, the ternary mixes of 50% GGBS and 7.5% silica fume did show improved air permeability at 44 days compared to the binary but by 91 days the binary concrete gave better results as the delayed reaction of the GGBS began to take effect. It is important to state that the effects of silica fume are significantly different to that of limestone or fly ash and are not covered in this study.

7.3 Relative Air Permeability to CEM I

By comparing the intrinsic air permeability of the blended mixes with CEM I, it is possible to see the overall influence of additions and w/c ratios, as well as test age effects on behaviour (shown in Figure 7.5). It was clear that air permeability increased with GGBS level, as noted in earlier studies by Elahi et al (*2010*). The lower 35% GGBS level gave the better result across the range of w/c ratio, improving with prolonged curing to 180 days, with the 10% limestone ternary concrete providing the lowest permeability results across the full range of

binary and ternary mixes and w/c ratio, except at the 35% GGBS level and at the lower w/c ratio.

The other limestone ternary mixes at the higher 55% and 75% GGBS levels gave much higher results relative to CEM I, increasing with GGBS level and addition percentage and with age. The air permeability of these mixes did, however, decrease with increasing w/c ratio when compared to CEM I. Tsivilis et al (*1999*) found that the mean pore size of a concrete is affected by limestone with the addition of 10% limestone to the clinker. This suggests a lower permeability, which also occurred in general across the range of ternary mixes but not when compared to the CEM I. However, as will be discussed further later, the critical pore size of the 10% limestone ternary cement paste is higher than the other combinations tested at both w/c ratios. This may suggest that the aggregate, being the only difference between them, has an effect on the permeation of the concrete notably in the region of the ITZ where the bond between the cement paste and aggregate is formed and where micro-cracking normally occurs (*Monteiro & Mehta, 2005*). Due to its inert properties, the limestone may reduce the bonding capability of the cement paste as well possibly creating weaker walls within the pore structure that collapse with the application of pressure. The aggregate itself is of low permeability and would only affect the area over which flow takes places (*Neville, 1995*).

The fly ash mixes gave higher results than the limestone and binary mixes at 28 days. By 180 days, the permeability had decreased with the difference more noticeable with increasing in w/c ratio. Given the increase in the limestone ternary mixes at 180 days, it is the fly ash ternary mixes that show a more improved permeability with age and also compared to their limestone counterparts at the 75% GGBS level.

The effects of fly ash on permeability are well covered within the literature with regards to their use as a binary addition. Even at these low addition levels, as a ternary material, the effects are evident with prolonged curing to 180 days given the delay in reaction that occurs. The effect of moisture content has already been discussed and the preconditioning of the test specimens should have removed moisture sufficiently to have avoided any influence on air permeability.

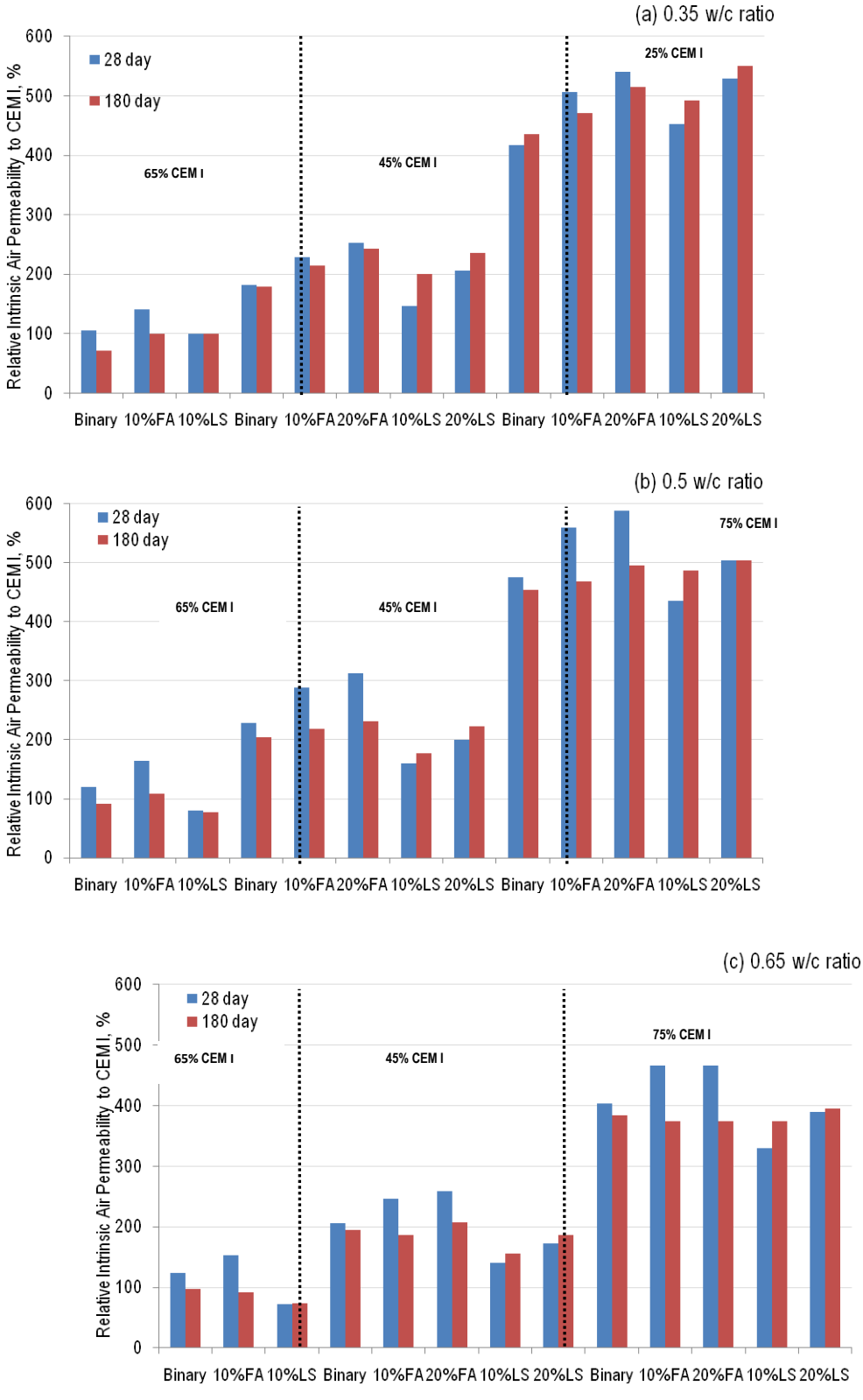


Fig 7.5 Intrinsic Air Permeability relative to CEM I

The aggregate within the concrete may also affect permeability and it is the aggregate that separates the permeability of a cement paste alone with that of concrete, as already noted. Types of aggregate may have differing permeability values, low permeability, as those used in this study, may reduce the effective area over which flow can take place. Unlike with cement paste the rate of flow in concrete is affected, as stated by Neville (*1995*), as it has to circumvent aggregate particles making its effective path longer, thus reducing permeability. As previously discussed, these aggregate particles are generally surrounded by hydrated cement paste forming the ITZ so this actual effect is minimal; in fact, in a well compacted concrete it is the permeability of the ITZ that can have the greater effect on the overall permeability of concrete (*Monteiro & Mehta, 2005*).

7.4 Water Penetration Under Pressure

The method involved clamping a 150mm cube test specimen into the testing station for 72 hours and application of pressure up to 500 KPa to a roughened surface, after which the depth of penetration is determined.

As with all previous tests a CEM I control sample was considered to provide a baseline with which to compare the binary and ternary blended concretes. At 28 days the lower 0.35 w/c ratio gave a reading of 10mm indicating the depth at which the water had penetrated at the set pressure over the 72 hour test period. As the w/c ratio increased to 0.5 and 0.65 the water penetration depth at 28 days increased to 17mm and 28mm respectively. By 180 days, the depth of penetration of the CEM I control mix had reduced across the range of w/c ratios to 7mm, 12mm and 19mm for 0.35, 0.5 and 0.65 w/c ratio respectively.

7.4.1 35% GGBS Level

It is evident from the data that an increase in w/c ratio increased the depth of water penetration of concrete as expected, which decreased following a longer curing period of 180 days.

At 28 days, the 35% GGBS binary mix gave the lowest depth of water penetration across the range of w/c ratios and was equal to the CEM I concrete at 0.5 w/c ratio, as shown in

Figure 7.6. All of the ternary mixes at this GGBS level gave higher results. At 0.35 w/c ratio, the 10% fly ash was the lower of the two ternary concretes and was only marginally higher than the CEM I control. An increase in w/c ratio to 0.5 and 0.65 indicated an improvement for the 10% limestone, with a depth of water penetration that was lower than its fly ash counterpart.

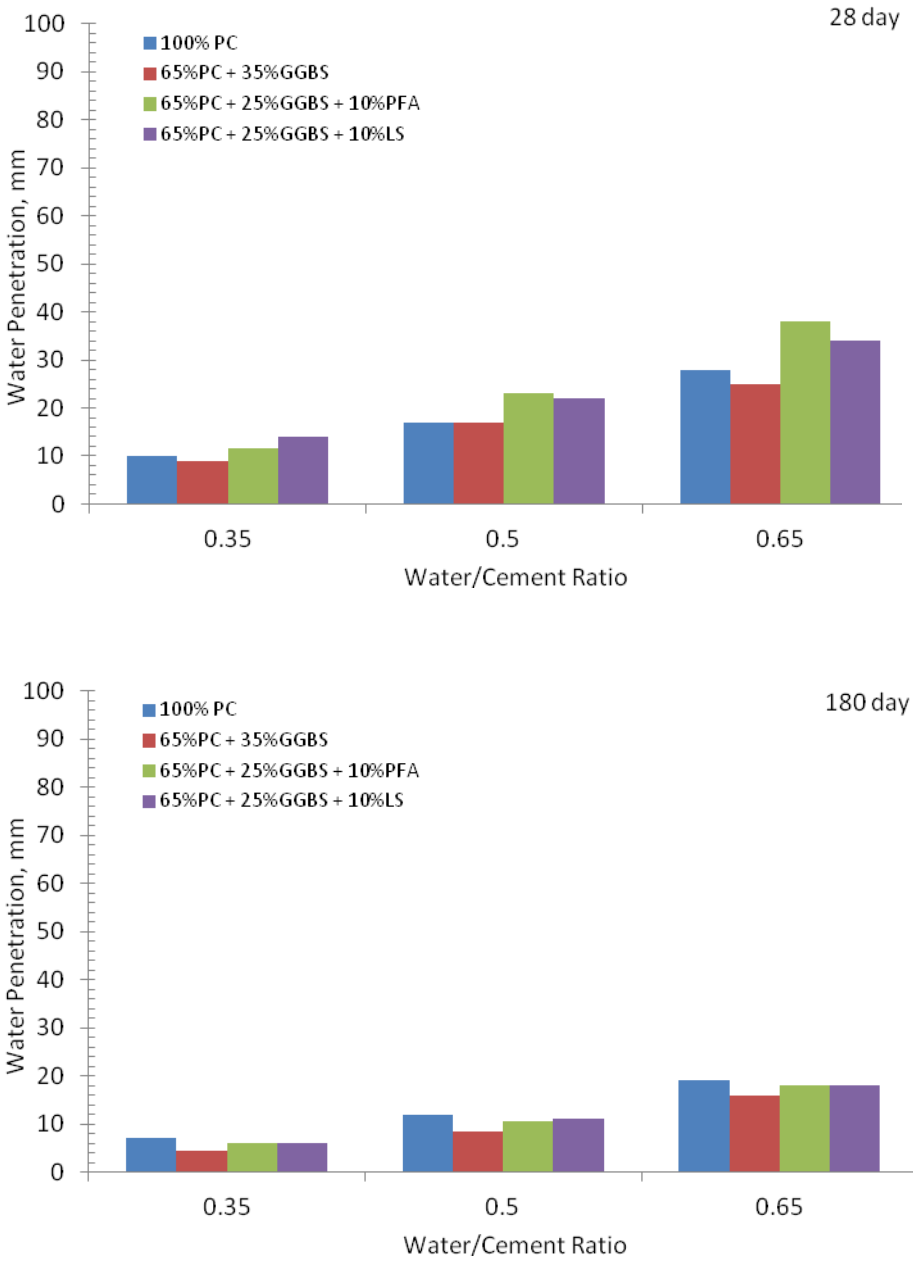


Fig 7.6: Water Penetration of 35% GGBS level concretes

By 180 days, a noticeable decrease was evident across the range of blended mixes and w/c ratios, especially with the ternary mixes. The binary mix remained the lowest of the blended concretes, but the longer curing time improved the effects of the ternary materials. Their results were more comparable and marginally lower than the CEM I control mix. A study carried out by Ramezanianpour et al (*2009*) into the influence of limestone cements found that in general an addition of up to 10% limestone can lower the depth of water penetration due to the filler effect. At 28 days this effect was not seen at this 35% level as the depth of water penetration remained high for both ternary mixes across the range of w/c ratios. Ramezanianpour et al (*2009*) discussed the effects of limestone used as a binary addition and suggested that as a filler it can modify the initial porosity of the concrete but when added as a ternary to GGBS concretes at this level the effects of the 10% limestone can be negative. Prolonged curing to 180 days allows for reaction by GGBS, thus increasing the C-S-H gel formation, filling the pore spaces more efficiently than the CEM I concrete.

7.4.2 55% GGBS Level

An increase in GGBS content showed a marked increase in the depth of water penetration. At this level, as shown in Figure 7.7, following 28 days curing, it is the CEM I control mix that gave the lowest depth of water penetration. The binary mix was higher but it is the ternary concretes that showed the highest increase in depth compared to the 35% addition level. At 0.35 w/c ratio the 10% and 20% fly ash ternary mixes were better than their limestone counterparts and equal to them at 0.5 w/c ratio. An increase to 0.65 w/c ratio, although increasing the depth of penetration in general, gave improved limestone ternary mixes compared to their fly ash counterparts.

By 180 days, the longer curing time had a significant effect on all mixes, most noticeably the blended concretes. Given the slower reactivity of GGBS this was expected. Just as the strength gain improved with prolonged curing, so did the permeability. The binary mix was the lowest of all mixes across the range of w/c ratios, with the reactivity of GGBS forming a denser micro-structure as more pore space is filled with C-S-H due to the greater proportion of silica, and reduced lime.

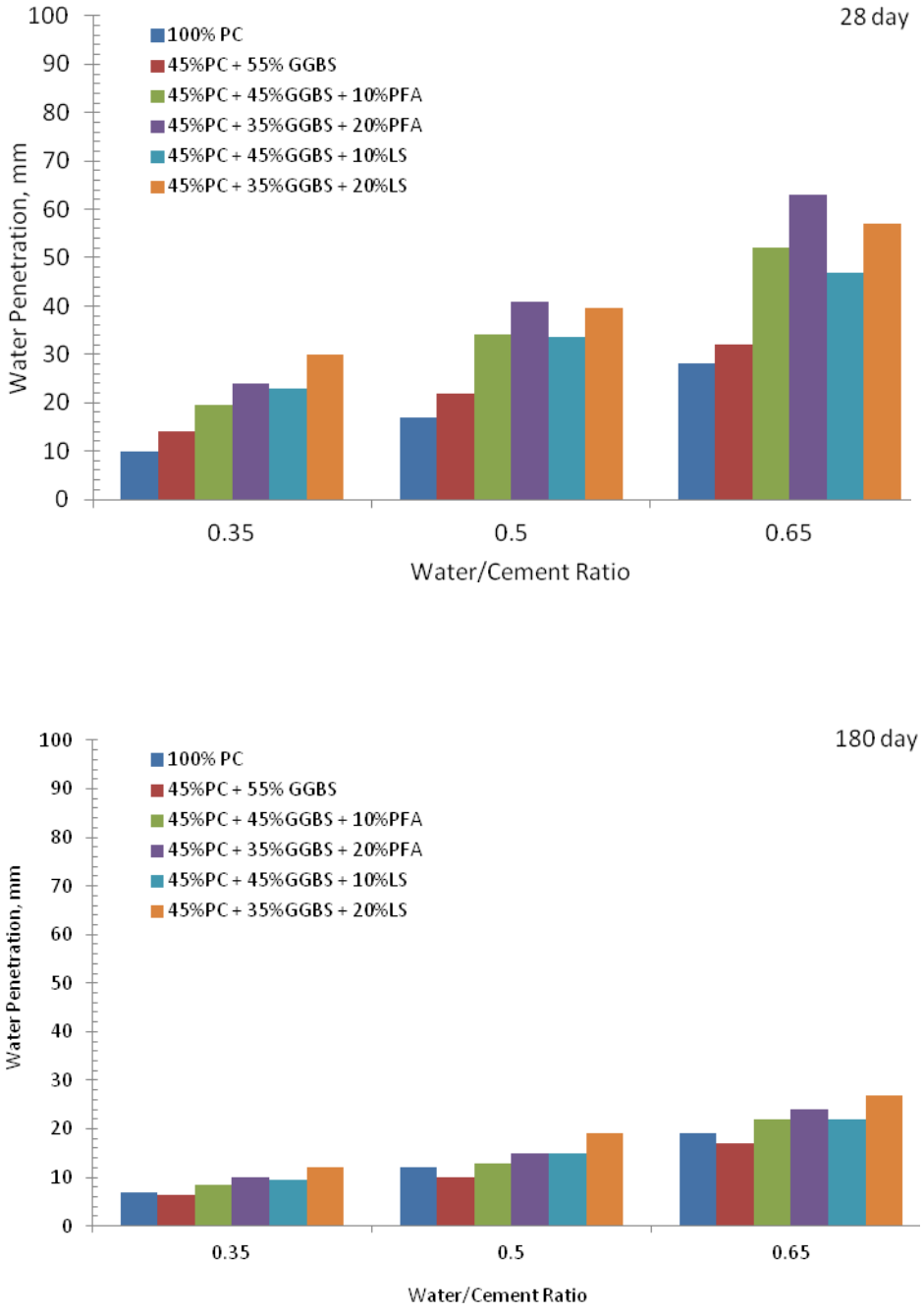


Fig 7.7: Water Penetration of 55% GGBS level concretes

The ternary mixes more than halved, in some cases, the depth of penetration. Whilst the ternary mixes still remained higher than the CEM I, the 10% fly ash ternary concrete was generally comparable with this and its limestone counterpart. At 0.35 and 0.5 w/c ratios, there was little difference seen between the 20% fly ash and the 10% limestone. The same study discussed earlier carried out by Ramezanianpour et al (*2009*) found that a greater addition of 20% limestone increased the depth of water penetration. The depth of the water penetration increased with w/c ratio as expected. Though the actual test parameters differed, similar trends were seen for both air permeability and water penetration tests at this GGBS level although the differences were not as obvious as those discussed earlier and shown in Figure 7.3.

7.4.3 75% GGBS Level

A further increase in GGBS content gave a more significant increase in the depth of water penetration with the difference between the CEM I control mix and the blended concretes more noticeable at 28 days, as shown in Figure 7.8. The binary and ternary concretes almost doubled in depth when compared to the 55% GGBS level. At 0.35 w/c ratio, both fly ash ternary mixes were lower than their limestone counterparts, but higher than the binary mix. At 0.5 w/c ratio the fly ash and limestone concretes were comparable. The 35% limestone was marginally higher than the 20% fly ash indicating that the filler effect was almost similar to the fly ash, which is likely to be competing for the free lime available. This is also seen with an increased w/c ratio to 0.65.

The 55% GGBS level illustrated improvements by prolonged curing to 180 days that were again noted at this GGBS level; although in this case all blended concretes were higher than the CEM I control mix. The 10% fly ash and the 10% limestone mixes were comparable across the range of w/c ratios, whilst the 20% fly ash was higher than both of these mixes, but still significantly lower than its limestone counterpart. The effects of the fly ash and limestone differ fundamentally in that the limestone acts as a filler, filling spaces between the GGBS and CEM I particles at lower replacement levels, indicated by a decrease in the water penetration, whilst at higher limestone levels dilution effects occur (*Ramezanianpour et al, 2009*). It has

been stated previously that the CEM I and GGBS hydrate/react, albeit at different rates, with the latter prolonged, but the limestone is considered not to have pozzolanic properties (*Sersale, 1992*) and the increase in limestone reduces the pozzolanic activity within the concrete.

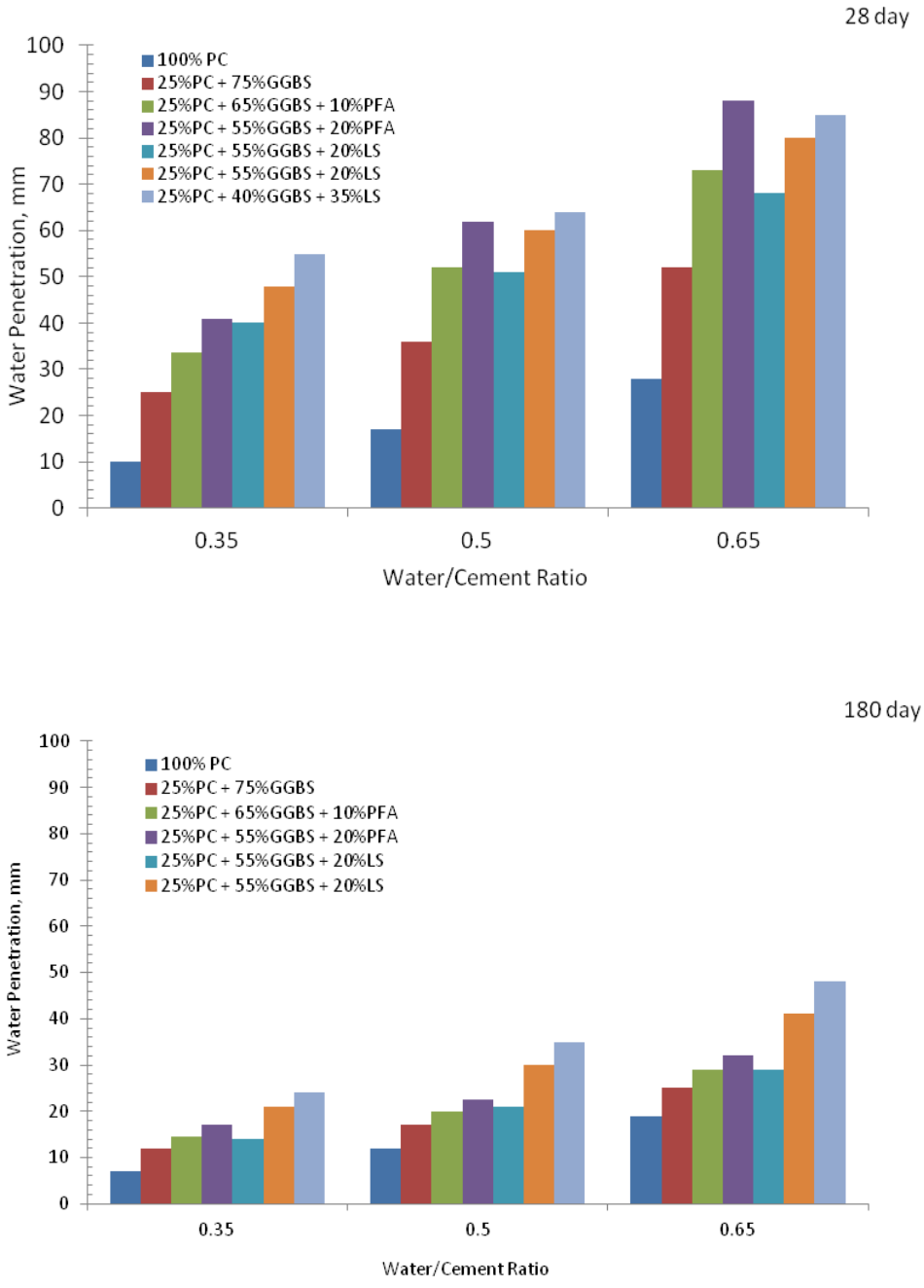


Fig 7.8: Water Penetration of 75% GGBS level concretes

The reduced water penetration of the fly ash ternary concretes, compared to those of limestone is due to its own pozzolanic reaction, despite competition for lime with the GGBS whose own reaction still occurs (indicated by continuing strength development) with time increasing C-S-H and therefore reducing pore space. Fraay (*1989*) attributed the reduction in capillary porosity of fly ash concretes to the products of the pozzolanic reaction diffusing away from fly ash particles, on which they form in the early stages, and precipitating within the capillary pores.

As well as both the dilution and filler effects, Irassar (*2009*) discussed heterogeneous nucleation occurring due to limestone particles acting as a nucleation site, increasing the early hydration of cement resulting in the production of a more disorientated crystallisation of CH. Heterogeneous nucleation is also discussed by Bonavetti et al in an earlier study (*2003*) and by Cyr et al (*2006*).

7.5 Relative Depth of Water Penetration to CEM I

By calculating the depth of water penetration of the blended concretes relative to the CEM I control mix, an overview of the results is presented in Figure 7.9; the effects of extended curing to 180 days is more prominent certainly for the lower 35% GGBS level across all three w/c ratios, where it is clear that all mixes were lower than the CEM I by 180 days.

It is also evident from Figure 7.10 the previously discussed dilution effect of the materials, as well as the individual properties of both the ternary additions and their effect within the mix. At the lower w/c ratio of 0.35, the fly ash was better than the limestone which improved with increasing w/c ratio. The depth of water penetration was lower at 0.65 w/c ratio (Figure 7.10 (c)) overall in relation to the CEM I concrete. The improvement of the limestone mixes with an increase in w/c ratio may be related to an increase in early hydration due to the previously discussed heterogeneous nucleation.

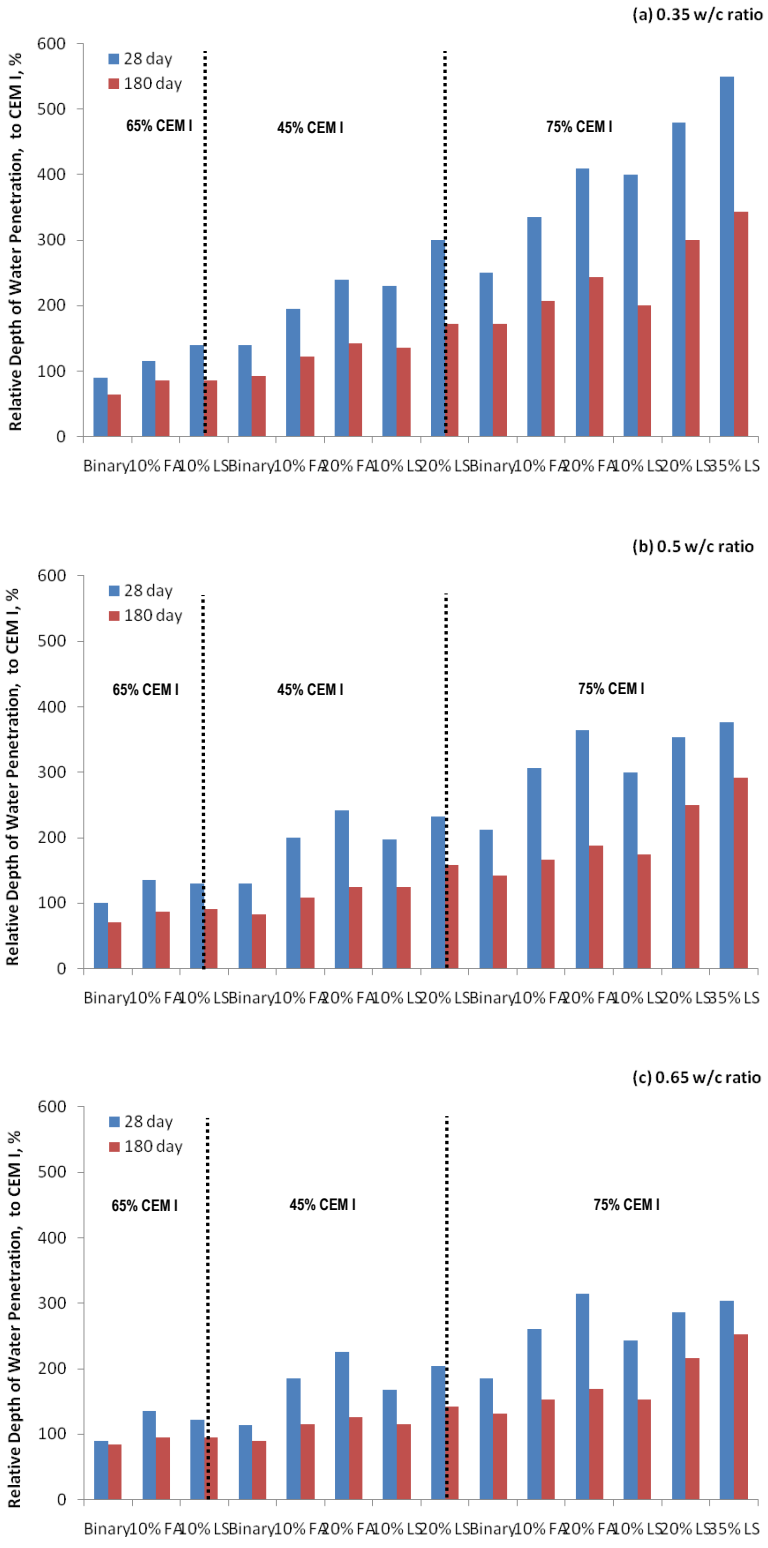


Fig 7.9: Relative Depth of Water Penetration to CEM I

7.6 Correlation Between Permeation Properties

Having examined air permeability and water penetration individually it was considered prudent to review them in relation to other properties thus far discussed. In relation to each other Neville & Brooks (*2007*) state that there is no unique relationship between two permeation properties, in respect of any concrete. When examined collectively by w/c ratio in Figure 7.10 it is seen that, especially for the higher w/c ratio of 0.65, there is a wide range/scatter of results. Similar patterns are seen for all three w/c ratios, albeit that the grouping is more condensed for the 0.35 w/c ratio, and whilst the R^2 value would indicate a reasonably strong correlation. However, when examined independently by addition and level of replacement, this is not necessarily the case.

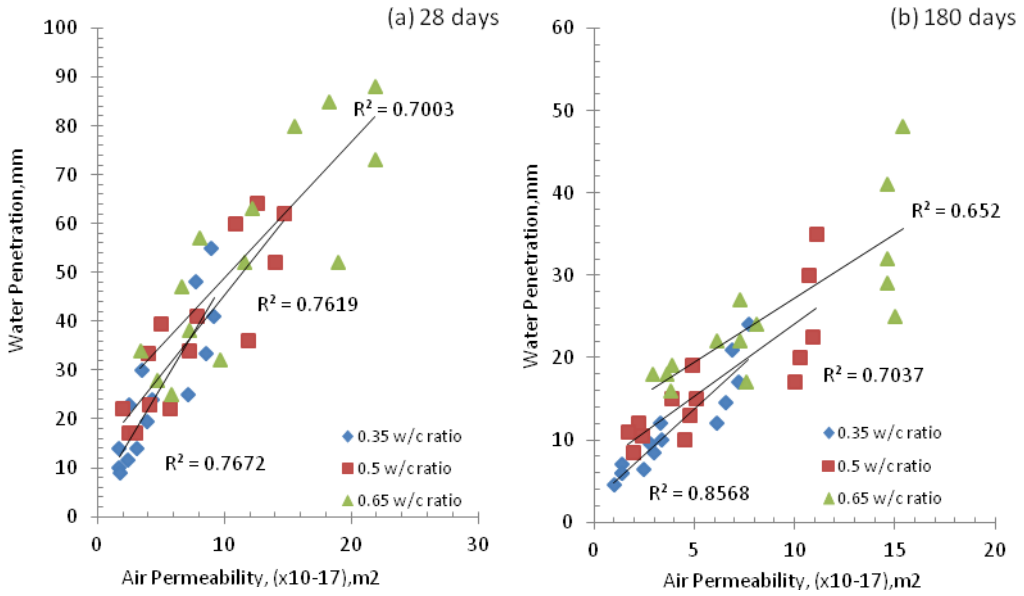


Fig 7.10: Correlation of tested permeability properties by w/c ratio at (a) 28 days and (b) 180 days

Concretes giving similar permeability results for air can give varying results for water penetration. For example, increasing fly ash addition from 10% to 20% for the ternary mixes at both 55% and 75% replacement levels had little impact on the air permeability results, but increased the depth of penetration. This trend is seen across all three w/c ratios, increasing with the proportion of mix water to material volume, at both test ages. For the limestone additions, both permeation properties are increased with higher levels of limestone. By 180

days, with increased levels of hydration, there is a notable grouping for each addition that is far less apparent at 28 days when hydration is still taking place within the concrete matrix. During this time it is likely that the pore system is continuously changing due to the cycle of narrowing and widening of pores as an effect of on-going physical and chemical interactions between the penetrating media and the minerals within the cement paste itself (*Mehta & Montiero, 2004*). The pressure, also associated with the tests may also have an effect on the pore structure. These effects are, however, unpredictable and merely indicative of the dynamics of the pore system.

7.7 Permeation v Compressive Strength

Within concrete it is the mix water that is considered to be indirectly responsible for the permeability of the cement paste. It is also, as discussed in previous chapters, related to the development of compressive strength. It would therefore be prudent to examine the compressive strength of the concretes in relation to their permeability properties. Collectively, and in general, it would appear that an increase in permeability would coincide with a decrease in compressive strength, as shown in Figures 7.11 and 7.12, for air permeability and water penetration respectively, the latter of which indicates a relatively strong correlation between the results for 0.35 and 0.5 w/c ratios, agreeing in part with Chidraprasit et al *(2007)*.

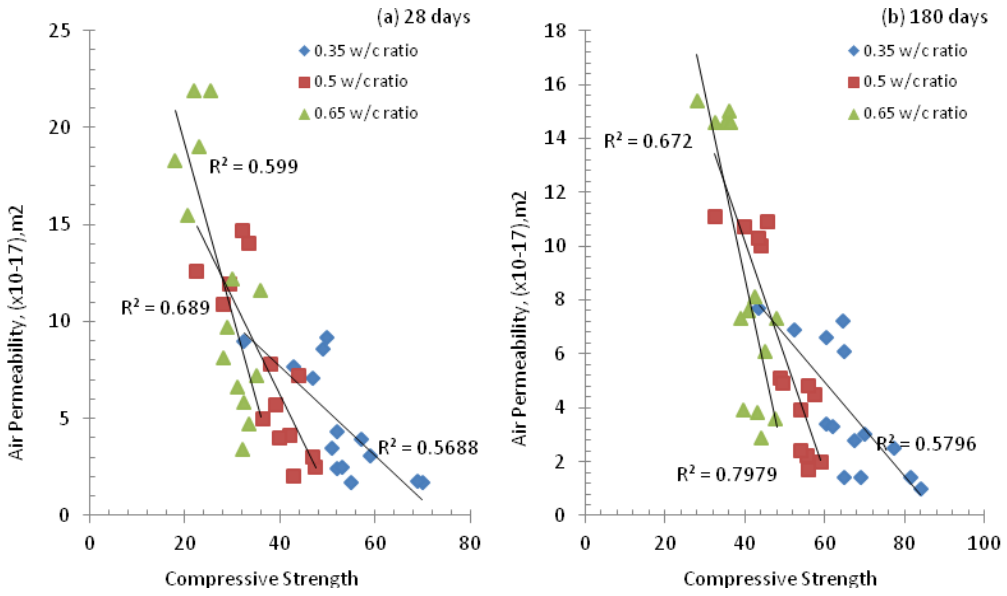


Fig 7.11: Air permeation against compressive strength by w/c ratio for (a) 28 days and (b) 180 days

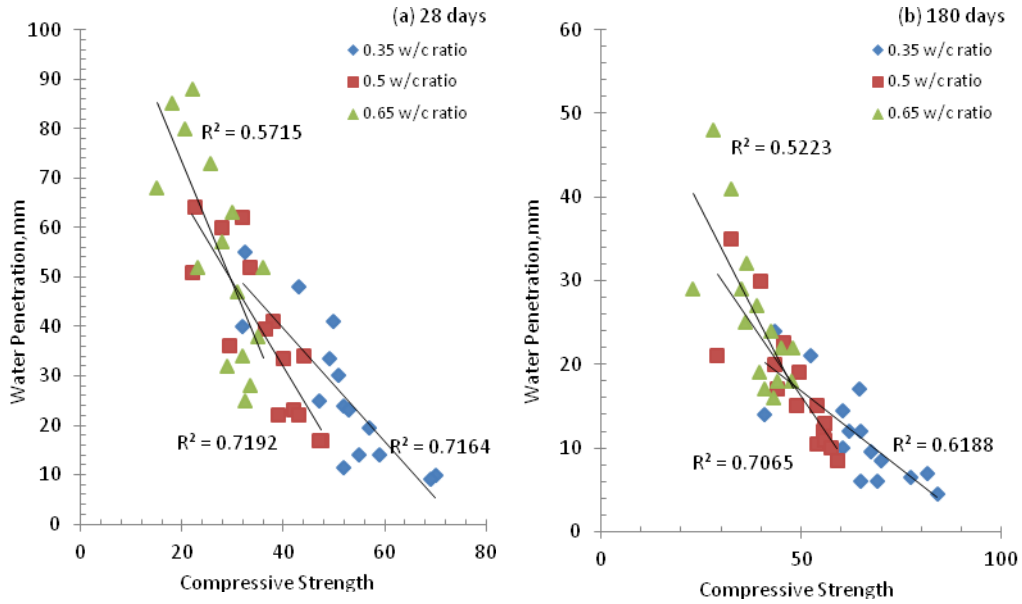


Fig 7.12: Water penetration against compressive strength by w/c ratio for (a) 28 days and (b) 180 days

The air permeability data appears to be more erratic than that of water penetration suggesting that there is a clear difference in the media and how it is transported within the concrete. Such differences, also noted with the absorption properties previously, may be due not only to the different media but to the differences in preconditioning. The samples for the air permeability tests are cored from 100mm cubes, approximately 50mm in length and oven dried to a constant weight. In the case of water penetration tests the entire 150mm cube is placed within the testing rig without oven drying. *Williamson & Clark* (*2001*) state that the near surface zone of the concrete can vary significantly in both composition and properties to the "heartcrete" zone that can extend to a depth of 50mm from the surface.

7.7.1 Permeation for Equivalent Cube Strength of 40 N/mm²

Given the discussed effect of mix water and therefore w/c ratio, on the strength and permeation properties of concrete these were examined in relation to the equivalent cube strength of 40 N/mm^2 as carried out previously with absorption data. In order to achieve an equivalent cube strength of 40 N/mm^2 at 28 days, the w/c ratio changes (as per Table 5.1), therefore the volume of material will differ whilst the mix water will remain constant at 165 l/m^3.

From Figure 7.13, showing the intrinsic air permeability for equivalent cube strength, it is clear from the results that the 10% limestone ternary, at the 35% level, provides lower permeability values at 28 days for the equivalent cube strength between mixes. This particular mix requires a w/c ratio of 0.5 corresponding with previously discussed data.

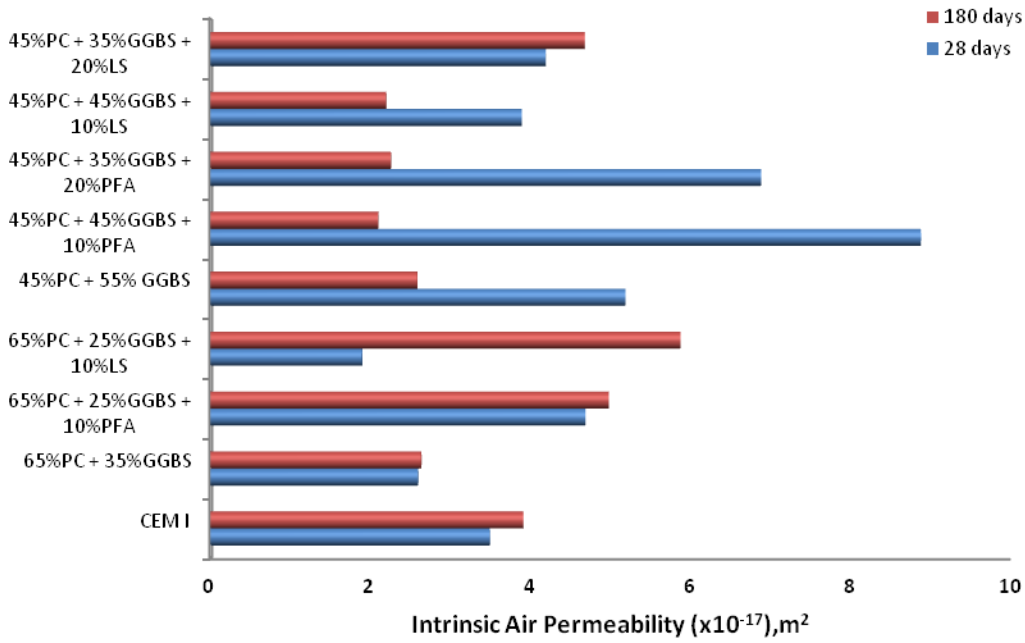


Fig 7.13 Intrinsic Air Permeability for Equivalent Cube Strength of 40 N/mm²

Figure 7.9 discussed earlier provides an overview of the effects of ternary additions, w/c ratio and longer curing times but these should be viewed in a more practical context especially if the depth of penetration is to be used as a quantitative assessment of the concrete. For a concrete to be considered impermeable, the depth of penetration should be less than 50mm, if the depth is lower than 30mm the concrete is considered to be impermeable under aggressive attack (*Neville, 1995*). Figures 7.6 and 7.9 indicate a number of test specimens that may be considered to be impermeable, or indeed impermeable under aggressive attack, but they do not take into consideration the strength of each individual specimen at either test age. In much the same way as Figure 7.13 does, Figure 7.14 illustrates the expected depth of penetration for each mix combination at the 35% and 55% GGBS level for equivalent cube strength of 40 N/mm^2. It is evident that all of these mixes can be

considered impermeable at 28 days by altering the w/c ratio to achieve equivalent strength and both ternary concretes at the 35% replacement level may be considered impermeable under aggressive attack. Given the consequences of poor permeability in resisting the ingress of attacking media, it would be fair to state that the development of improved permeability properties at the earliest age possible is greatly advantageous.

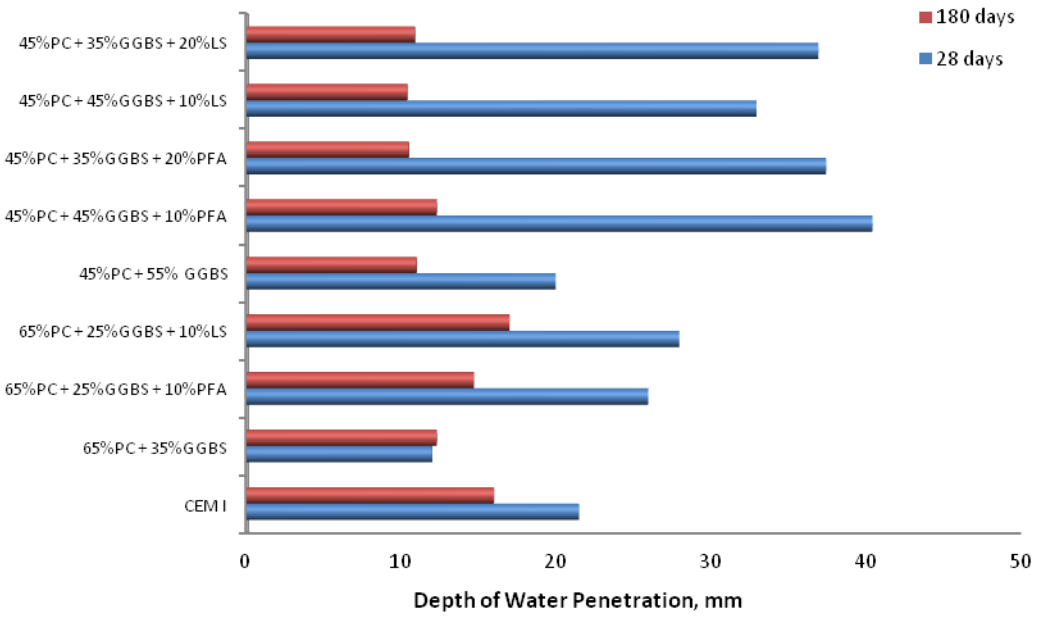


Fig 7.13: Depth of Water Penetration for Equivalent Cube Strength of 40 N/mm²

7.8 Permeation v Porosity

Whilst it is possible to gain some understanding of the transportation properties of concrete itself, it is difficult to determine what Mehta & Monteiro state as a 'fluid transport property factor' due to the effect of changes that are unpredictable in the pore system, notably the structure of pores, upon penetration of attacking media (*Mehta & Monteiro, 2004*). It was stated previously that the mix water is indirectly responsible for the permeability of concrete. More specifically the hydrated cement paste due to its content determining the total space followed by the unfilled space after the mix water has been consumed by both the hydration reactions and evaporation to the environment.

Neville & Brooks (*2007*) state that the permeability is governed by cement paste and porosity but this relationship is not as simple as the pore size distribution is a factor. In addition the pore structure itself is fundamental (*Massazza, 1996; Chia & Zhang, 2002*). In this respect, and as per previous chapters, the porosity of selected cement pastes will be considered in relation to the permeability of their concrete counterparts. Figures 7.14 and 7.15 provide an overview of the data of the permeation properties tested, together with the critical pore diameter. This indicates that some similarities can be seen between them and those for the absorption tests shown in Chapter 6 (refer to Figures 6.13 and 6.14).

When examined in more detail, in order to determine if any correlation exists between the data, it is clear that the critical pore diameter relates more to water penetration than air permeability, as shown in Figures 7.16 and 7.17 respectively. In general, water penetration increases with critical pore diameter across both w/c ratios and test ages. This trend is seen, to a similar extent, with air permeability at the 0.5 w/c ratio, but the correlation is weak and there is a more erratic spread of data.

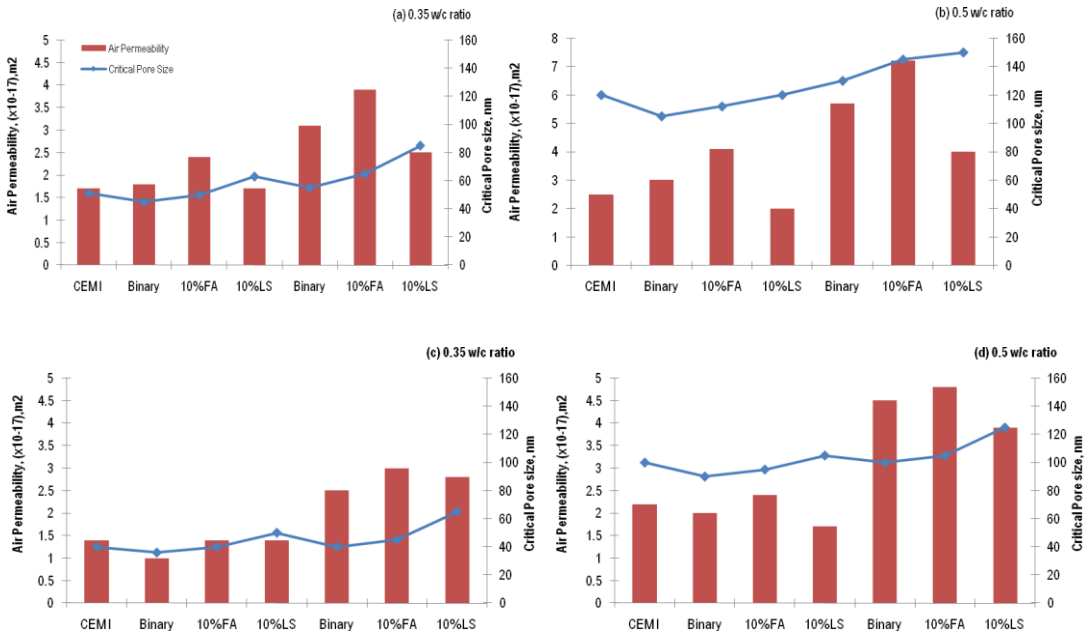


Fig 7.14: Air permeability against critical pore size at 28 days [(a) and (b)] and 180 days [(c) and (d)]

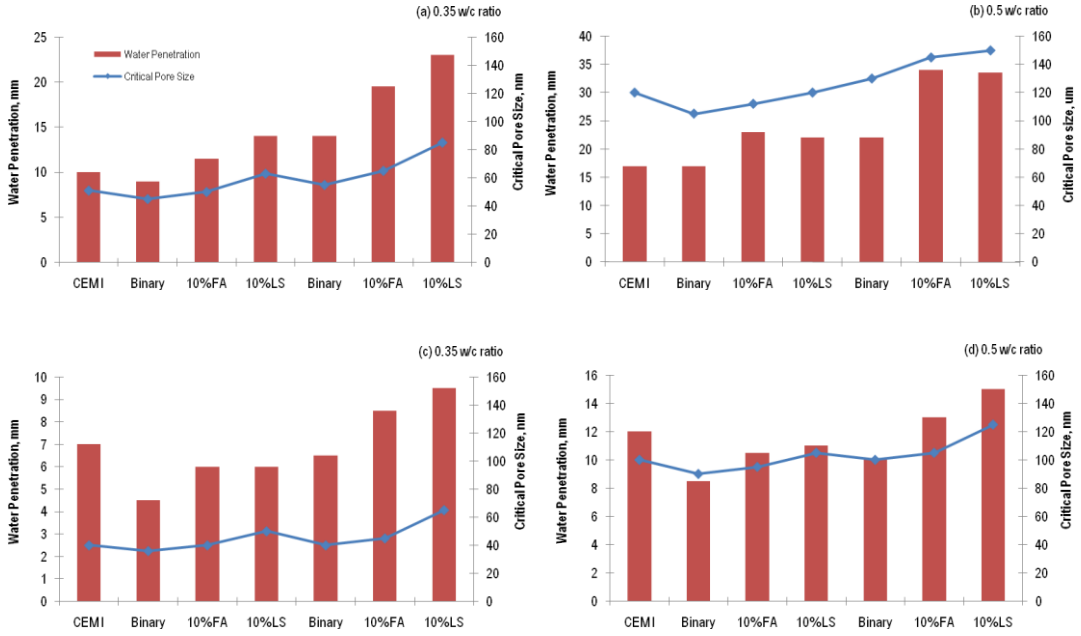


Fig 7.15: Water penetration against critical pore size at 28 days [(a) and (b)] and 180 days [(c) and (d)]

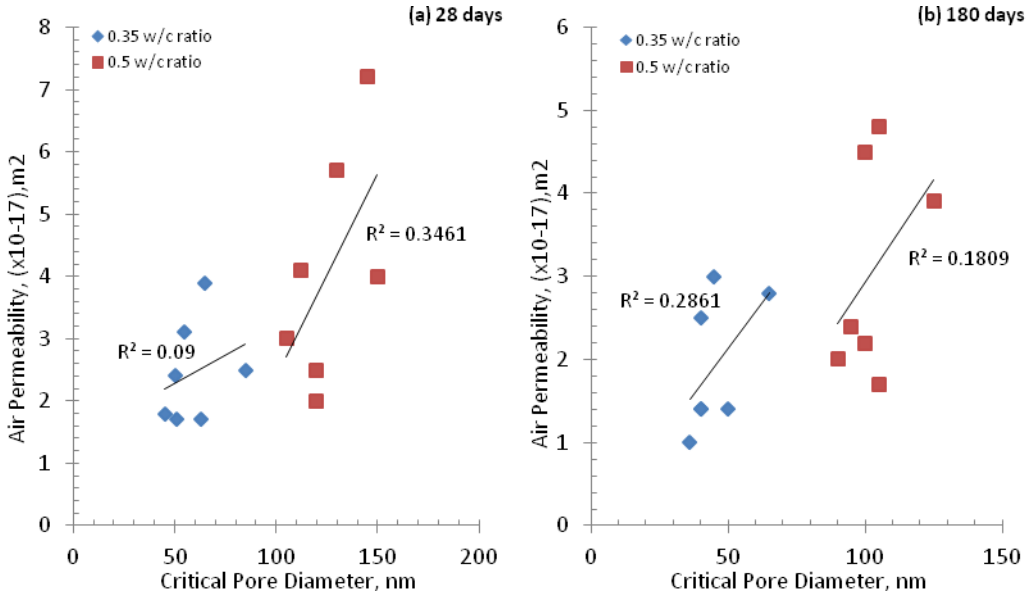


Fig 7.16: Air permeability against critical pore diameter for both w/c ratios at (a) 28 days and (b) 180 days

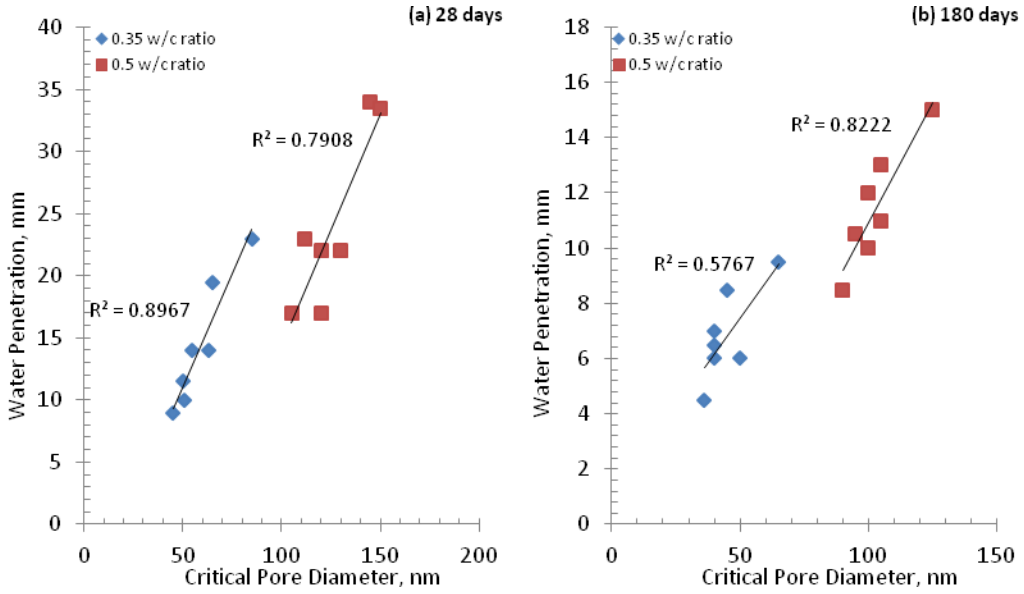


Fig 7.17: Water penetration against critical pore diameter for both w/c ratios at (a) 28 days and (b) 180 days

The data, when compared with total porosity, gives very poor correlations for both permeability properties tested as shown in Figures 7.18 and 7.19. A number of mixes gave similar total porosity results but both water penetration and air permeability readings varied in spite of this. At 28 days, the data was wide spread but by 180 days, for the water penetration test, it is evident that hydration and slowed, if not ceased entirely, and the effects of the additional materials were noted. Whilst generally they reduce the total porosity marginally, compared to the CEM I control mix, the 10% fly ash ternary at the 55% replacement level gave higher water penetration results as did the limestone ternary at this level, with slightly higher porosity also obtained. Pore blocking effects may have occurred with the discontinuity of pores also happening within the matrix, but this would be noted due to the differences in permeability results, where it is likely that weaker pores walls within the ITZ will break down due to the applied pressure.

The mercury intrusion porosimetry tests were carried out on cement paste and not concrete samples and therefore do not take into consideration the porosity effect of the aggregates used in the concrete or the ITZ. The effects of the aggregates were discussed earlier. Elahi et al (*2010*) noted that varying fine and coarse aggregate could affect permeability as much the effects of additional material on the microstructure (*Elahi et al, 2010*). The effect

on the ITZ has also been discussed by Mehta & Monteiro (*2006*) and Basheer et al (*2005*). The actual effects of the fine and coarse aggregates in this instance are supposition and worthy of greater study in the future, but whilst the ITZ is likely to have some effect a relationship between the two may be expected

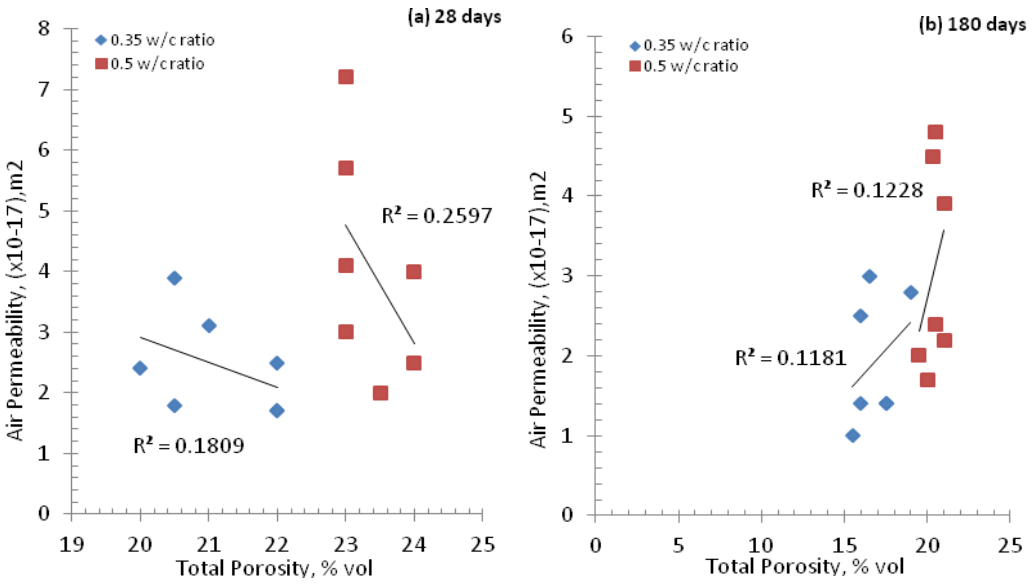


Fig 7.18: Air permeability against total porosity for both w/c ratios at (a) 28 days and (b) 180 days

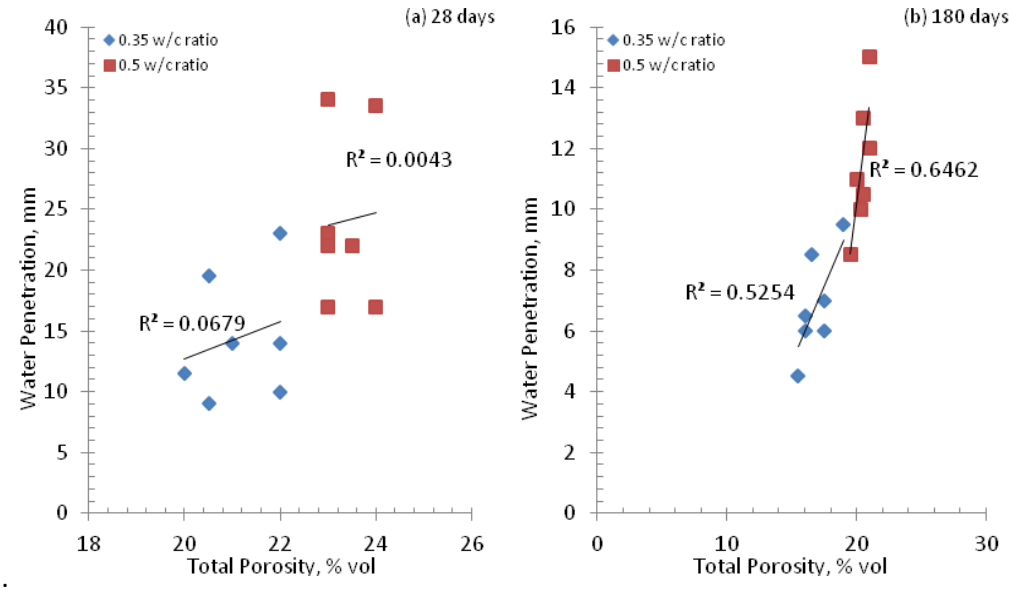


Fig 7.19: Water penetration against total porosity for both w/c ratios at (a) 28 days and (b) 180 days

7.10 Summary

As with the absorption tests discussed in Chapter 6 it was found that permeability increased with a rise in w/c ratio and GGBS level and decreased with prolonged curing to 180 days.

The binary mixes at the lower 35% GGBS level, across the range of w/c ratio gave lower air permeability results than at higher addition levels. Though they were slightly higher at 28 days, the delayed and prolonged reaction of GGBS, given the extended curing time, improved the microstructure due to increased C-S-H in the gel pores reducing permeability (*Neville, 1995*). This improvement was also seen in the water penetration tests. Unlike the air permeability values the 55% level also showed improvements with prolonged curing in the binary concretes, but not at the 75% level.

The addition of fly ash did little to improve the permeability of concrete at the 0.35 and 0.5 w/c ratio. An increase to 0.65 w/c ratio and prolonged curing did improve the fly ash ternary concretes when compared to binary mixes and, indeed, CEM I concrete at the lower 35% level. Similar trends were indicated in the water penetration results apart from those at the increased w/c ratio, improvements were seen with time at the lower 35% GGBS level when compared with the CEM I concrete but it was slightly higher than the binary concrete. An increase in fly ash content to 20% had the effect of increasing permeability values was possibly due to increased competition with GGBS for the lime.

The 10% limestone ternary concretes showed encouraging results for air permeability at the lower 35% level. Across the range of w/c ratio at 28 days, it gave consistently lower values which improved further with prolonged curing. However, increasing the GGBS level increased air permeability which was further increased for the 20% limestone ternary concrete suggesting a diluting effect. This was also noted in the water penetration tests.

Despite Neville & Brooks (*2007*) implying that no ‘unique’ relationship exists between air permeability and water penetration a correlation was noted which was likely to be due to them both being dependent on the w/c ratio. In addition the relationship between compressive

strength and permeability generally showed that strength increased with decreasing permeability confirming that the pore porous matrix is indeed weaker.

No correlation was found between the permeability properties and the porosity of the cement paste indicating that the effect of aggregate on permeation properties and that of additional materials varies; a slight correlation was noted for the water penetration tests at 180 days. It was also noted that a greater relationship existed between water penetration and critical pore diameter than porosity, or indeed between air permeability and critical pore diameter.

The depth of water penetration increases with critical pore size. For the binary mixes, as the replacement level increased the critical pore size increased, slightly but the increase in air permeability was more pronounced, with an increase in w/c ratio. An increase in ternary addition had the same effect, however the permeability of fly ash was higher than the limestone but had a lower critical pore size, whilst the limestone was higher in critical pore size and lower in air permeability.

CHAPTER EIGHT: CARBONATION & CHLORIDE INGRESS OF CONCRETE

8.1 Introduction

In addition to the strength requirements of concrete relevant to structural and fire resistance, it is also important to consider durability which has received greater consideration over the last 20 years or so. Indeed, the final location of a concrete structure needs to be taken into consideration as this can provide a range of exposure conditions. BS EN 206-1:2000 covers exposure classes as summarised in Table 8.1 and includes not only attack from carbonation in a variety of situations (dry, cyclic wet and humid) but also from chlorides. Chlorides may be in the form of spray, or direct contact with sea water, or from other sources such as those in de-icing salts. BS EN 206-1:2000 also includes freeze/thaw attack for concretes in moderate and high saturation situations. This is not covered in this study but shows the extent of environments that need to be considered.

The absorption and permeability properties and the movement of gases and fluids through concrete were discussed in earlier chapters. The integrity of the concrete can alter due to interactions with the constituents and the pore fluid including absorbed chlorides, sulfates and CO_2, which can affect the concrete itself and that reinforced with steel (*Basheer et al, 2005*). The majority of concretes structures will be reinforced and it is this reinforcing steel that is the most vulnerable from both carbonation, in the form of gas, and chloride ingress. Structures in urban environments are more at risk due to high concentrations of CO_2 in the atmosphere (*Sisomphon & Franke, 2007*). Yoon et al (*2007*) discussed the continued increase in CO_2 in the atmosphere due to global climate change since the 1970's.

Fabbri et al (*2009*) refer to the effects of underground CO_2 sequestration on concrete reservoirs, which given certain temperature and pressure conditions cause CO_2 to be in its

supercritical form, or fluid state. Yet carbonation alone does not represent a risk to concrete itself, unless the concrete is reinforced where there is a potential risk to corrosion of the steel thus threatening the structural integrity of the concrete structure and this is more likely to be an issue of surface damage. Chloride ingress again threatens the durability of concrete in a similar way to carbonation, causing corrosion of steel reinforcement which may not necessarily be due to the surrounding concrete being visibly damaged but also due to the permeability of concrete. Threats from salt environments can range from extreme exposure with immersion in sea water, although this tends to be reliant on the presence of oxygen, to that from salt spray in coastal regions, or from de-icing salts during winter conditions that brings with it additional issues, e.g. freeze-thaw cycles. Given the importance of the durability of concrete selected mixes were tested with regard to their resistance to chloride ingress and carbonation.

Table 8.1: Exposure classes summarised from BS EN 206-1:2000

Class Designation	*Environment*
No risk of corrosion or attack	
XO	Concrete without reinforcement or embedded metal all exposures except where there is freeze/thaw, abrasion or chemical attack
Corrosion induced by carbonation	
XC1	Dry or permanently wet
XC2	Wet, rarely dry
XC3	Moderate humidity
XC4	Cyclic wet and dry
Corrosion induced by chlorides other than from sea water	
XD1	Moderate humidity
XD2	Wet, rarely dry
XD3	Cyclic wet and dry
Corrosion induced by chlorides from sea water	
XS1	Exposed to airborne salt but not in direct contact with sea water
XS2	Permanently submerged
XS3	Tidal, splash and spray zones
Freeze/thaw attack with or without de-icing agents	
XF1	Moderate water saturation, without de-icing agent
XF2	Moderate water saturation, with de-icing agent
XF3	High water saturation, without de-icing agent or sea water
XF4	High water saturation, with de-icing agent or sea water

Due to the restricted time available and given that both processes in a natural exposure take considerable time, accelerated tests were used to establish the resistance of concrete to carbonation and chloride.

8.2 Carbonation

Accelerated carbonation tests were carried out on selected concretes. Previous studies *(Sisomphon & Franke, 2007; Osbourne,1986)* have established the poor resistance to carbonation of GGBS concretes and thus the aim of the work described in this section was to establish whether the addition of ternary materials can improve this. Carbonation is the result of dissolution of CO_2 in the concrete pore fluid, reacting with calcium hydroxide and calcium silica hydrates (CSH) to form calcite. It is the formation of calcium carbonate ($CaCO_3$) by chemical reaction in the concrete. The creation of $CaCO_3$ requires three equally important substances: carbon dioxide (CO_2), calcium phases (Ca) and water (H_2O). CO_2 is present in the atmosphere in varying degrees depending on location (rural or urban), calcium phases (mainly $Ca(OH)_2$ and CSH) are present in the concrete and water is contained in the pores.

The CO_2 diffuses through the pore spaces, where the first reaction occurs with the H_2O to form carbonic acid (H_2CO_3) which then reacts with the calcium phases.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

[Eq 8.1]

$$H_2CO_3 + Ca(OH)_2 \rightarrow C_2CO_3 + 2H_2O$$

[Eq 8.2]

Once the $Ca(OH)_2$ is converted and is missing from the cement paste hydration products in the form of CSH ($CaO{\cdot}SiO_2{\cdot}H_2O$) will then liberate CaO which will also carbonate:

$$H_2CO_3 + CaO \rightarrow CaCO_3 + H_2O$$

[Eq 8.3]

The $Ca(OH)_2$ is the most reactive with CO_2, turning to carbonic acid in the presence of moisture. The calcium carbonate ($CaCO_3$) produced during the reaction is insoluble and its production will

cease unless free CO_2 is present in the water when a further reaction will occur to produce soluble bicarbonate (*Mehta & Monteiro, 2006*).

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

[Eq 8.4]

This reaction is reversible and requires an amount of 'balancing' CO2 to maintain equilibrium. It should, however, not be confused with bi-carbonation which is a separate process that can occur in concrete with very high w/c ratio due to formation of hydrogen carbonate ions at pH levels lower than 10. Contrary to normal carbonation, bi-carbonation will result in increased porosity making the concrete soft and friable. It can be recognised within the microstructure by the presence of large 'popcorn' like calcite crystals as well as the highly porous paste (*Concrete Experts International, 2006*).

The pH value will begin to fall once these reactions have taken place, from pH 12.5/13 for normal concrete to around pH 9 for carbonated concrete (*Yoon et al, 2007*). The carbonation of the concrete alone is not, essentially, debilitating. However, once the process has reached the reinforcement and the pH value has dropped below 13 the passive 'film' on the steel reinforcement is compromised and corrosion will ensue. As both Basheer et al and Papadakis state, the majority of concrete deterioration is due to corrosion of reinforcement due to carbonation induced depassivation of steel bars (*Basheer et al, 1996; Papadakis, 2000*).

The rate of carbonation is not a linear function, changing with time and depth. It is a natural process and in good quality concrete it is very slow with an average penetration depth of 1mm per year. The speed of the process through concrete is mainly dependent on two parameters: the permeation and calcium content of the concrete as well as the ambient atmospheric conditions, which includes the concentration of CO_2, relative humidity (RH) and temperature. With regards to the permeability, the process has a continuing need for CO_2 from the atmosphere, for carbonation to spread fresh CO_2 from the surface needs to be supplied continuously, penetrating deeper into the concrete. Low porosity and permeability will decrease the rate of CO_2 ingress therefore delaying carbonation which generally occurs in the pores at a relative humidity between 40% and 90%. At a lower RH CO_2 cannot dissolve in water, while if this is higher than 90% it is not able to enter the pore system.

Despite having an adverse effect on the degree of concrete alkalinity and its ability to protect reinforcement the physical effects within concrete are usually positive. Carbonation of mature concrete densifies its structure, increases strength and reduces permeability, however, it does increase shrinkage in concrete that is mature, causing additional cracking.

In CEM I concrete it is only the reaction of $Ca(OH)_2$ and CO_2 that affects the rate of carbonation. With blended concretes the process of carbonation is more complex. In concretes containing GGBS there is a lower level of $Ca(OH)_2$ which is more likely to be completely carbonated. Once this has happened carbonation will take place with the CSH that is produced at a greater rate in concrete containing GGBS or fly ash. Higher levels of $CaCO_3$ are produced, exacerbating carbonation further and consequently pores with a larger diameter than 100nm are created. It is these pores that aid carbonation.

The test samples were placed in a carbonation tank with an enriched 4% CO_2 environment at 20^oC and a humidity of 50% ± 5%. The purpose of the accelerated carbonation test is to reduce the normal period of carbonation from many years to a few weeks *(Sisomphon & Franke, 2007)*. Osbourne *(1986*) reported on the importance of the curing regime on concretes containing GGBS, suggesting that poorly cured concrete can cause high carbonation. As discussed in Chapter 3, all samples were cured in water at a controlled temperature of 20^oC ± 1^o for 28 days. The carbonation specimens were then removed and laboratory dried for two weeks before being coated with wax, leaving one face open. A phenolphthalein 1.0% ethanol indicator solution was applied to the split and cleaned surface of the concrete. If the surface turns purple the pH is >8.6, where it remains colourless the pH of the concrete is <8.6 suggesting carbonation. Fully carbonated concrete has a pH of approximately 8.4, a pH of 8.6 may be indicated by a faint pink colour where a strong, immediate colour change will be indicative of a pH higher than 9 or 10.

The tests were carried out over a period of 20 weeks and the results are reported in Figure 8.1, which shows a comparison of 8 and 20 week results across the range of w/c ratios. It was evident, as with previous tests, that an increase in w/c ratio increased the rate of carbonation. Carbonation also increased with GGBS level at 8 weeks and further with the ternary additions, which was more noticeable with the fly ash ternary concretes at the later, 20

week, test age. The reactions are much slower at the greater GGBS level, leading to reductions in binding of CO_2, due to the dilution of $Ca(OH)_2$ within the mix. At this age (8 weeks) the amount of calcium hydroxide (CH) within the GGBS concretes is limited compared to that of CEM I, resulting in the CO_2 not becoming fixed near the concrete surface leading to little, or no, pore blocking formation of calcium carbonate (*Khan et al, 2002; Thomas & Matthews, 1992*). Given that it is stored in a dry environment it is unlikely that more CH will form. It is the content of CH and rate of CO_2 penetration that Shi et al state as the two key factors controlling carbonation (*Shi et al, 2009*).

The addition of fly ash in ternary concrete increased the rate of carbonation, with significant increases seen in these concretes by 20 weeks across the range of w/c ratios. Shi et al also concluded that both fly ash and GGBS decreased carbonation resistance confirming earlier studies by Kahn et al (*2002*) and Sisomphon & Franke (*2007*) who studied longer-term carbonation effects and determined that a 50% addition of fly ash to a CEM III-B (blast-furnace slag cement) increased the depth of carbonation compared to CEM III-B concrete. By testing concretes following 3, 7 and 28 days curing, Sisomphon & Franke also found that increased curing improved carbonation resistance (*Sisomphon & Franke, 2007*). At 20 weeks testing, it is clear that the GGBS binary concretes gave reduced carbonation depth compared to the ternary concretes, Shi et al (*2009*)attribute this to the GGBS being generally more active than the fly ash creating a slightly lower CH content and a denser matrix (*Shi et al, 2009*).

Given the continued hydration of the GBBS (indicated by the later strength development of the concretes), it was expected that all samples would show an increase in carbonation depth with time. In the case of the limestone ternary mixes this occurred rapidly during the first five weeks after which the initial rates slowed but carbonation depth still increased as shown in Figure 8.2, which illustrates the rate of carbonation for limestone ternary concretes as 0.5 w/c ratio over the 20 week test period. The 10% limestone ternary mix at the 55% level appeared to increase at a slightly greater rate. The CEM I concrete gave the best results for resistance to carbonation over the test period. This may be due to the amount of $Ca(OH)_2$ present in the concrete; a lower concentration increases carbonation depth, whilst a higher concentration decreases carbonation (*Bier, 1987*). The 20% limestone ternary concrete

at the 55% addition level gave improved resistance to carbonation depth compared to the other ternary concretes.

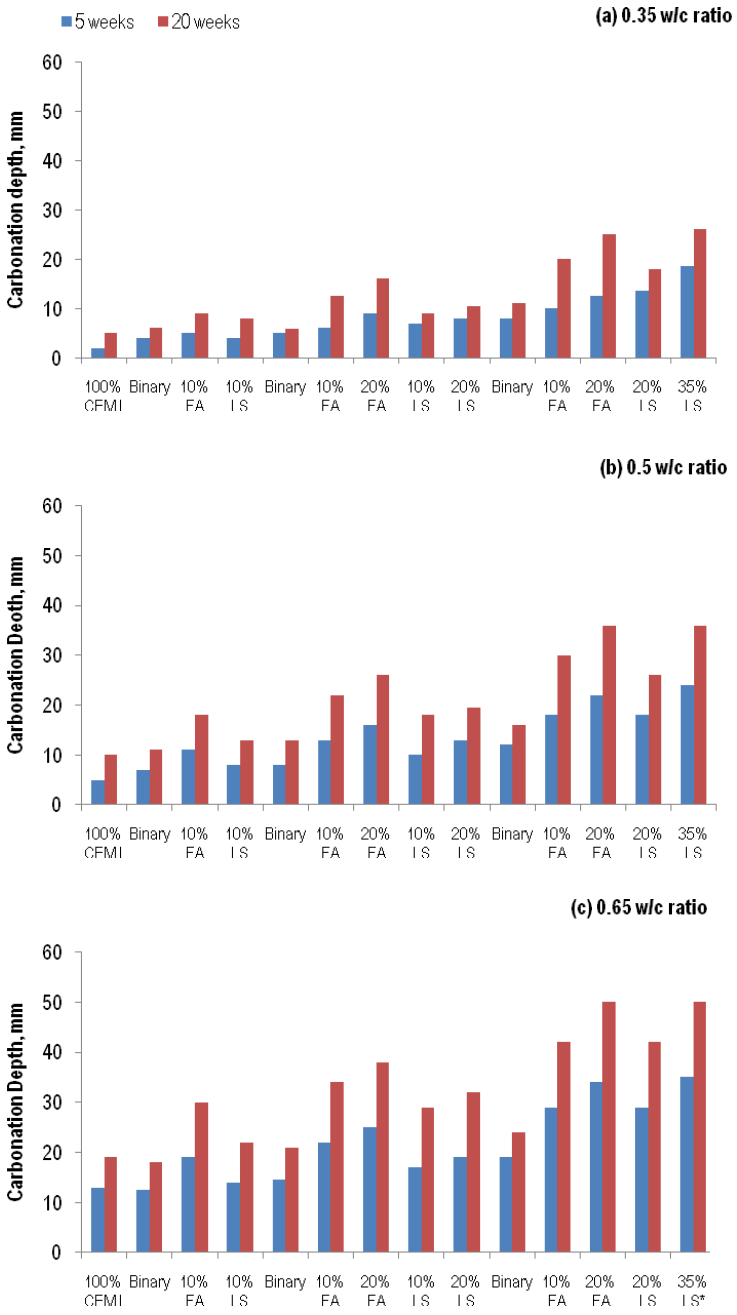


Fig 8.1: Carbonation depth at 8 and 20 weeks across the range of w/c ratios.

(35% LS* recorded depth at 16 weeks)

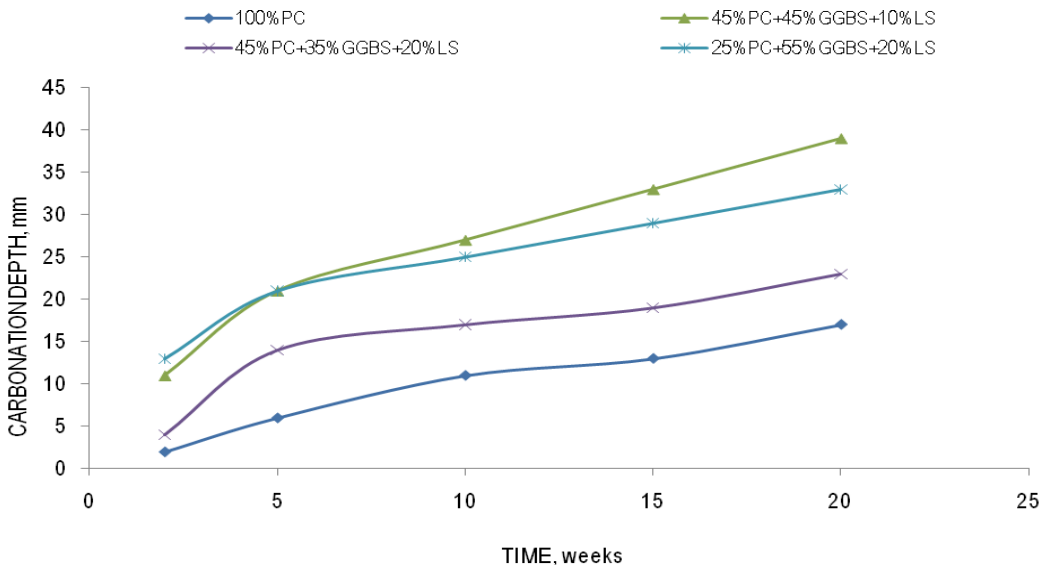


Fig 8.2: Carbonation for limestone ternary mixes at 0.5 water cement ratio

The rate of carbonation for the fly ash ternary mixes in general did not seem to slow during the first 10 weeks, as shown in Figure 8.3. The increased rate of carbonation, as discussed previously, due to the addition of fly ash was expected. Sisomphon & Franke (*2007*) suggest this to be a result of the lower levels of $Ca(OH)_2$, as indicated by Bier (*1987*), in the hardened cement paste caused by silica in the fly ash reacting with $Ca(OH)_2$ from the hydration of the cement. Sisomphon & Franke (*2007*) tested CEM III-B concretes together with a CEM III-b + 50% fly ash mix following 3, 7 and 28 days curing under water. In line with the results from this study, the CEM I control mix remained the most resistant to carbonation, compared to other mixes, both CEM III-B + 50% fly ash and CEM I + 50% fly ash.

The rate of carbonation in both the 45/35/20 limestone and 25/55/20 limestone ternary mixes appeared to slow after the initial five weeks, but this was not seen in the fly ash ternary mixes. This supports the findings of Fraay et al (*1989*) who reported that slag-fly ash concrete had the poorest performance, which is consistent with the slower hydration and development of the pore systems. The effects of limestone on carbonation resistance are contrary to other, earlier reported tests. Where previously it was seen that a 10% addition of

limestone was more effective in reducing air permeability or water penetration in Chapter 7, and an increase to 20% was detrimental, it was evident from Figure 8.1 that 20% limestone, especially at the 55% GGBS level was of benefit. Despite high initial carbonation during the first five weeks, the rate slowed significantly from 10 weeks onwards, with a difference of 5-7mm between the CEM I and ternary mix. This initial increase indicated in the first five weeks may possibly be due to heterogeneous nucleation with the addition of $Ca(CO)_3$ from the limestone accelerating the hydration and producing a more disorientated crystallisation of CH affecting the porosity of concrete, as discussed by Irassar (*2009*). The amount of CH within the GGBS cement paste is limited compared to the CEM I as discussed previously. It may also be due to the dilution effect whereby a volume of 20% inert filler replaced the GGBS content thus reducing, or delaying, the reaction and hydration of the cement structure further, as there is less GGBS to consume lime. With regards to these tests specimens further hydration or reaction is unlikely to have occurred since removal from the curing tank and drying for 2 weeks.

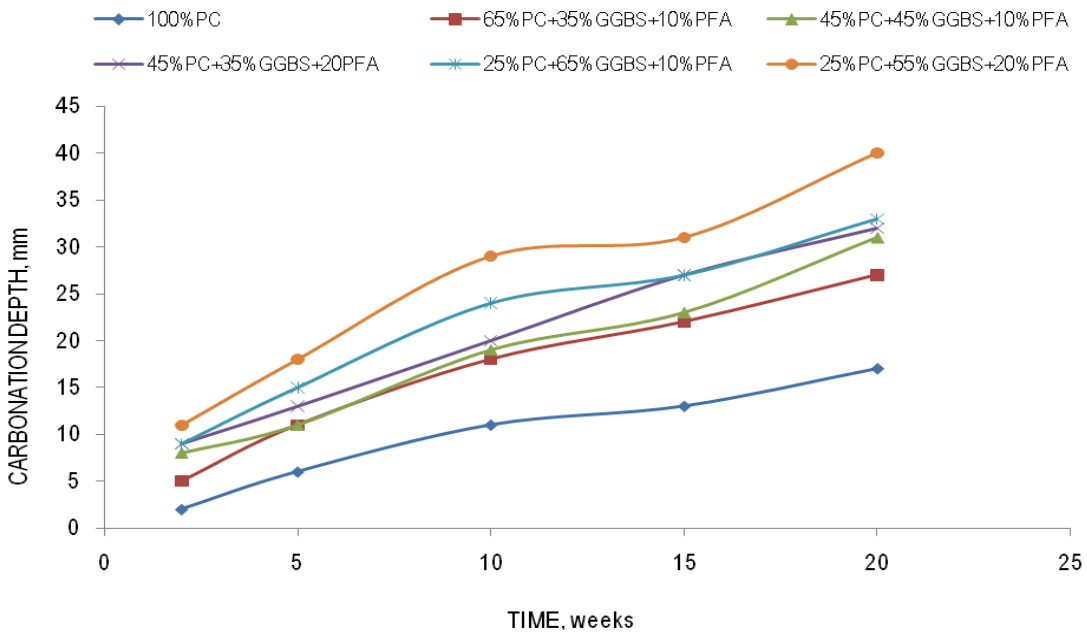


Fig 8.3: Carbonation for PFA ternary mixes at 0.5 water cement ratio

8.3 Carbonation in Relation to Tested Concrete Properties

8.3.1 Strength

Strength is considered to be a general indicator of the durability of concretes due to having similar influencing factors, such as the type of cement and w/c ratio. Shi et al (*2009*) state that strength and carbonation are related, together with air permeability and the pore structure of the concrete matrix (*Shi et al, 2009*). Given the range of combinations considered it is appropriate to examine these relationships. Figure 8.4 shows a general relationship between the depths of carbonation, measured at 5 weeks against compressive strength of concretes at 28 days (the 5 weeks test age is closest to that of the 28 days test of the compressive strength).

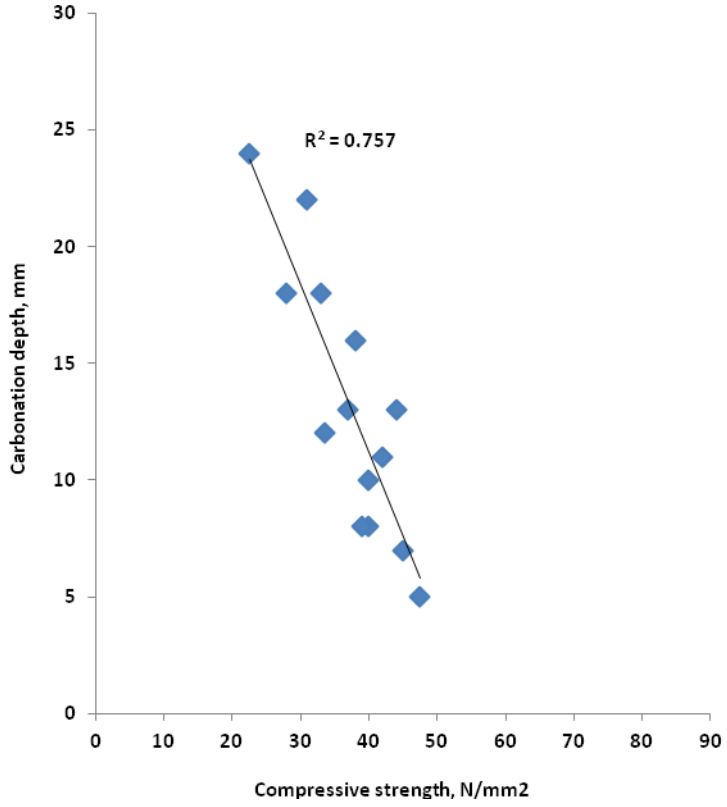


Fig 8.4: Level of carbonation (5 weeks) in relation to compressive strength (28 days) at 0.5 w/c ratio.

In general it is seen that carbonation resistance increases with compressive strength. In addition it is shown in Figure 8.5 how the w/c ratio can also affect the durability of the concrete in order to achieve an equivalent strength of 40N/mm^2. The w/c ratio is altered for each mix

depending on the volume of the constituent materials, as discussed previously in Chapter 5. Of interest are the binary and ternary mixes at the 55% replacement level that show a lower level of carbonation then the CEM I control at an equivalent strength of 40N/mm^2 at 28 days. The w/c ratio is 0.08 lower than the CEM I and it is the higher w/c ratio that may cause bi-carbonation as discussed previously, that can occur at higher w/c ratios. Whilst the binary at the 75% replacement level does give better results the addition of ternary materials exacerbates carbonation though not to the same extent as those at the lower, 35% replacement level. For the ternary mixes, again, this may be due to the higher w/c ratio, in addition fly ash has similar effects to those of GGBS, increasing CSH production and therefore higher $CaCO_3$. However, there is little difference between the 20% and 10% fly ash ternary concretes at the 55% replacement level, with a slight decrease shown by 180 days. As before, this may be due to a lower w/c ratio required for equivalent strength. At higher replacement levels, it is the influence of the GGBS that has an adverse effect on the carbonation of the concretes.

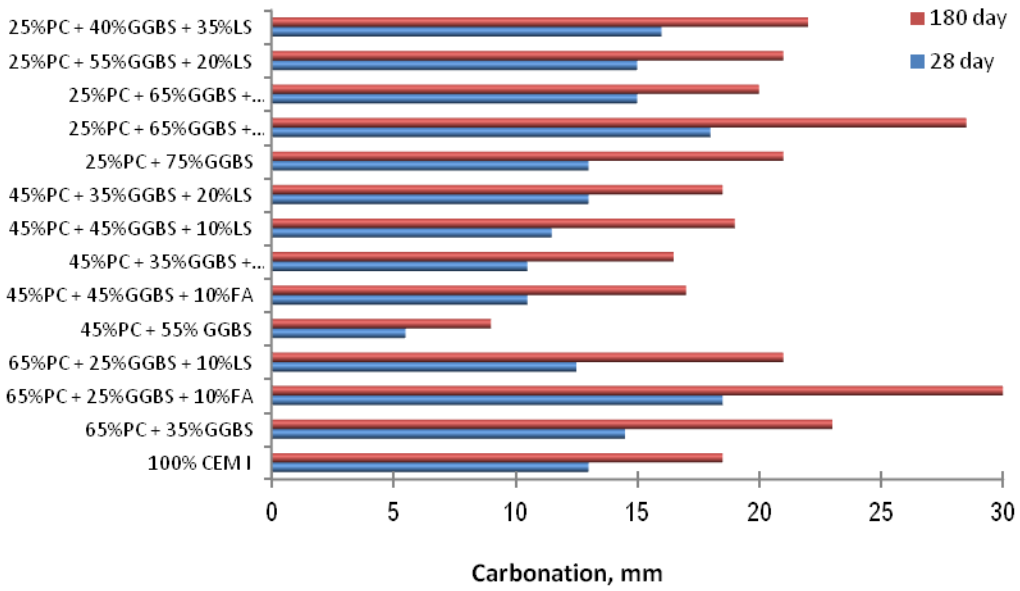


Fig 8.5: Level of carbonation for equivalent strength of 40Nm.

8.3.2 Porosity

Shi et al (*2009*) discussed the role of porosity of concrete and its influence on strength. It was stated that the threshold and mean diameter of the pores, together with their tortuosity is related to carbonation and air permeability. In this respect, as a rule, both strength and carbonation are dependent on different pore structure parameters (*Shi et al, 2009*). With this in mind, Figure 8.6 shows the depth of carbonation at 5 weeks against the critical pore diameter for selected cement combinations at 0.35 w/c ratio (Figure 8.6a) 0.5 w/c ratio (Figure 8.6b) at 28 days whilst Figure 8.7 illustrates the total porosity. It is clear that no correlation is indicated for 0.35 w/c ratio critical pore size and there is no relationship indicated between porosity and carbonation for the differing materials. Whilst the concretes may have similar critical pore diameters or total porosity, the level of carbonation can differ. It is clear from this that it is not only the pore structure that affects the rate of carbonation but the constituent materials themselves. For the lower w/c ratio, the higher levels of carbonation were obtained at higher 55% replacement level. For the 0.5 w/c ratio, it is the fly ash ternary blends that give the greater depth of carbonation, despite having differing critical pore diameter and similar porosity.

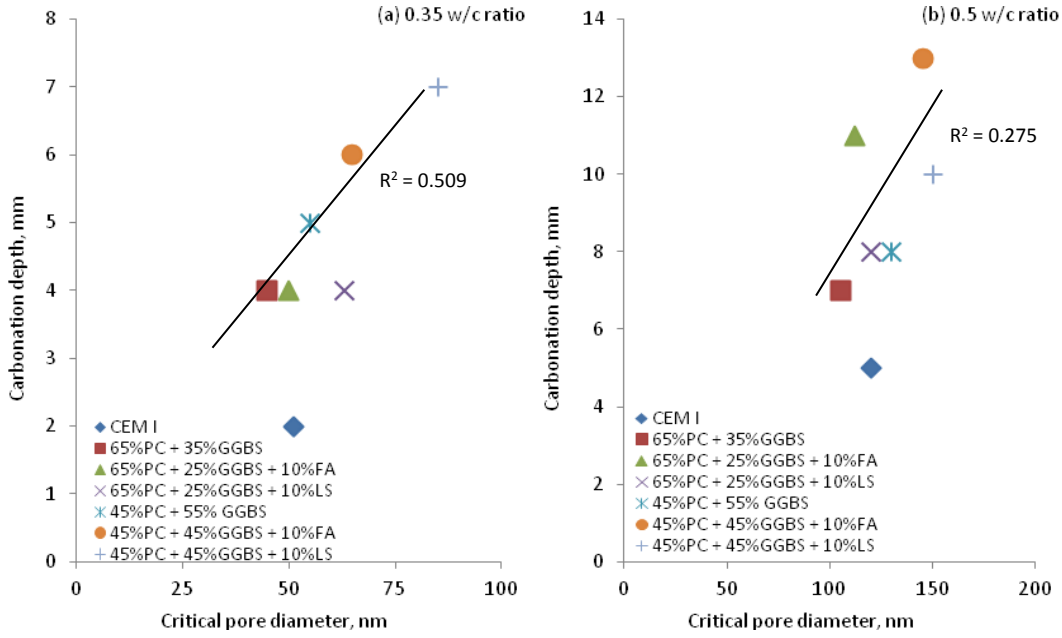


Fig 8.6: Level of carbonation (5 weeks) in relation to critical pore diameter at 28 days for (a) 0.35 w/c ratio and (b) 0.5 w/c ratio

As indicated earlier, both GGBS and fly ash contribute to the increased rate of carbonation, due to the lower levels of $Ca(OH)_2$ which will completely carbonate (*Mehta & Monteiro, 2006*). The high levels of CSH produced by these blends will provide further sites for carbonation. However, if the depth of carbonation was examined in relation to the voids ratio, shown in Figure 8.8 a much stronger correlation can be seen but it should be remembered that the voids ratio is calculated based on the dry mix and does not consider the effects of water and, hence, hydration.

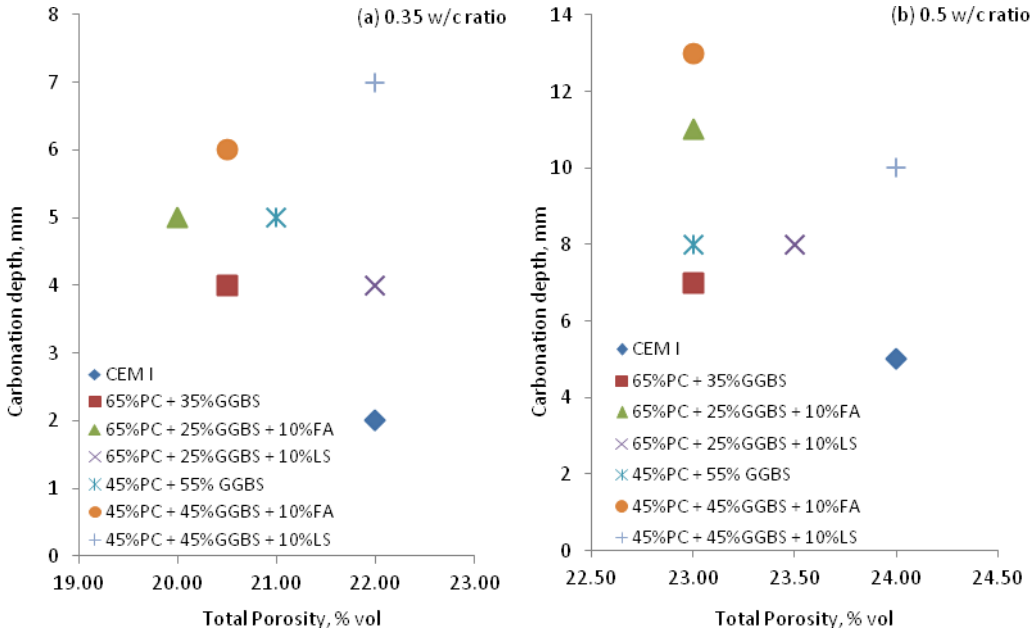


Fig 8.7: Level of carbonation (5 weeks) in relation to total porosity (%, vol) at 28 days for (a) 0.35 w/c ratio and (b) 0.5 w/c ratio

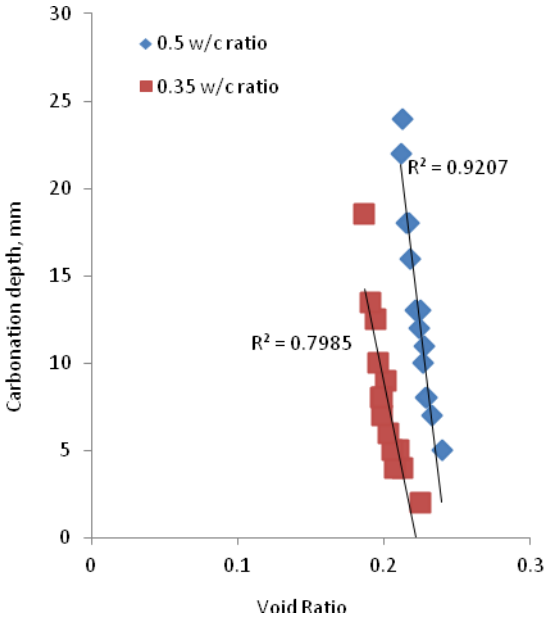


Fig 8.8: Carbonation depth against voids ratio.

8.3.3 Permeation and Absorption

It was noted earlier that there is a relationship between permeability and carbonation of concrete observed by Shi et al (*2009*). Given that the rate of carbonation depends on the permeation of atmospheric CO_2 to enter the concrete matrix, this is not unreasonable and was therefore examined in this current study, as shown in Figure 8.9, where the carbonation depth at 5 weeks (indicating only the early stage of exposure) is plotted against the intrinsic air permeability at 28 days for the 0.5 w/c ratio group of mixes. It was clear that a correlation exists for a given addition, whether binary or ternary, in that an increase in air permeability increased the depth of carbonation as a general rule. This confirms the relationship between the two noted by Dhir et al (*1989*) and later by Ramachandran & Beaudoin (*2001*). The fly ash ternary concretes show higher depths of carbonation against air permeability than their limestone counterparts. Whilst this illustrates further the poor performance of fly ash reported by Bijen et al (*1989*), it also indicates that both the depth of carbonation and air permeability are affected by physical and chemical properties of the cement and additions as is well known and covered in numerous earlier studies. Figure 8.10 also indicates a correlation with the ISAT data. From this it may be determined that the transport mechanisms differ the effects of the materials and their hydration products are similar in both cases, as previously discussed.

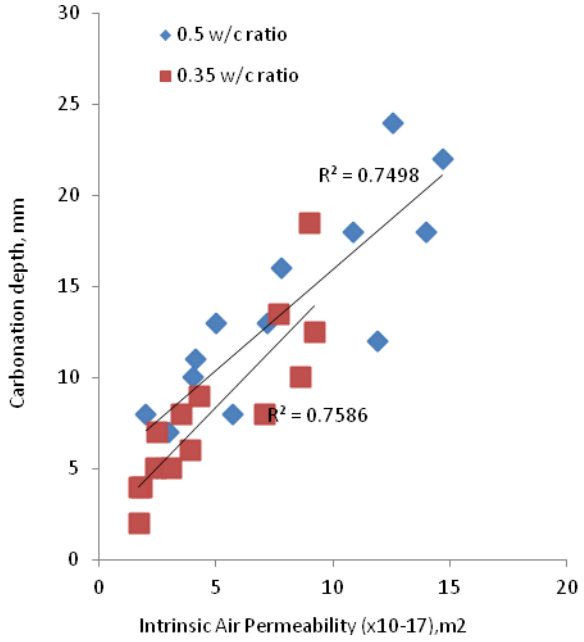


Fig 8.9: Depth of carbonation (5 weeks) against intrinsic air permeability (28 days)

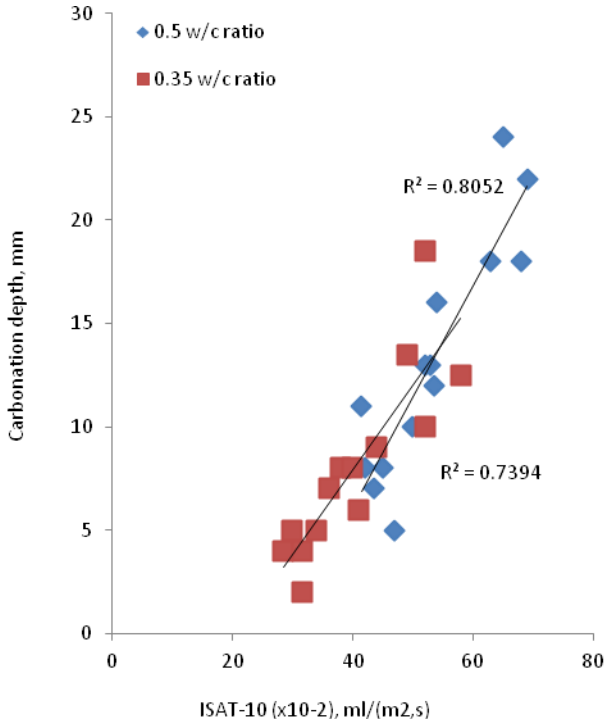


Fig 8.10: Depth of carbonation (5weeks) against ISAT at 28 day

It is apparent that the rate of carbonation differs depending on the exposure type or location. Whilst this particular test method used is accelerated (in a 4% CO_2 enriched environment) the highest that a specific natural exposure may reach is 1% (*Detweiler et al, 1996*). In highly populated urban areas, it is possible that CO_2 concentration may reach 0.3%, whilst in rural areas this can be as little as 0.03% (*Sisomphon & Franke, 2007*). It is also the moisture content of concrete that can affect the carbonation rate. The test samples were placed in an environment with a relative humidity of 50% when the rate of carbonation is said to be at its highest. Detweiler et al (*1996*) suggest that a relative humidity of 40% may actually stop the rate of carbonation. With regards to the permeability of GGBS concrete Bouikni et al (2009) stated that a lower permeability can often ensure that the rate of carbonation is confined to the initial 10mm, slowing further penetration down considerably and providing protection to the steel reinforcement. Sisomphon & Franke (*2007*) stated that a cover depth of 30-35mm should be recommended to avoid corrosion of steel rebar in reinforced GGBS concretes. Table 8.2 indicates the minimum required depth for cement types outlined in both BS8500 and BSEN206 where the minimum cover recommended ranges from 15 to 35+Δc depending on cement type.

Table 8.2: Comparison of exposure classes and requirements from BS 8500 and BSEN206

Exposure Class	**XC1**		**XC2**		**XC3 or XC4**				
	BS8500	**EN206**	**BS8500**	**EN206**	**BS8500**				**EN206**
Minimum Strength Class[a]	C20/25	C20/25	C25/30	C20/25	C25/30	C28/35	C32/40	C40/50	C30/37
Maximum w/c ratio	0.7	0.65	0.65	0.65	0.65	0.6	0.55	0.45	0.65
Minimum Cement Content (kg/m³)	240	260	260	260	260	280	300	340	300
Minimum Cover to reinforcement (mm)	15+Δc[b]	15+Δc	25+Δc	25+Δc	35+Δc	30+Δc	25+Δc	20+Δc	20+Δc
Permitted Cement Type	All	CEM I	All	CEM I	All cement types except CEM IV/B[c]				CEM I

[a] C20/25: 300x100mm cylinder / 150mm cube compressive strength (N/mm²)

[b] Δc = acceptable tolerance to accommodate fixing precision, typical range 5mm-15mm

[c] PC with fly ask content of 36-55%

8.4 Chloride Ingress

Chloride attack can be caused by de-icing salts or sea water. With regards to the latter, it is important to note that this may not be due to direct contact with sea water but the result of airborne droplets that can travel up to 2 miles given the right environmental conditions. De-icing salts, though necessary, can cause more physical damage, by the way of salt scaling, than chemical, as they are used to treat horizontal surfaces that are prone to freeze-thaw and can be more damaging due to the types of salts commonly used ($NaCl_2$ and $CaCl_2$) (*Neville, 1995*). These effects are not considered here but illustrate additional influences of chloride on durability. As with carbonation, chloride ingress does not directly affect concrete, but the steel reinforcement of the structure will corrode should the concrete cover become permeable and chloride build up in sufficient quantities at this locations. Transportation of chloride ions occurs through pore solutions of the concrete by a number of mechanisms. Diffusion is the result of a concentration gradient and can be described by the diffusion coefficient. Migration in an electric field and water flow will be determined by the ionic mobility. In addition, pressure gradients may cause water flow and in partially dry concrete, absorption is likely to occur, as well as wick action. Despite the multi-mechanism phenomena, each process will be affected by the pore structure and the interaction between ions in the pore solution and the pore walls, namely chloride binding and membrane effects which will be discussed in more detail later in this chapter. Additionally pore blocking can occur when entrapped or entrained air voids can block the pore solution transportation of ions, yet promote gaseous transportation. One of the benefits of GGBS as a material in cement is its ability to refine the pore structure hopefully mitigating this effect.

Omar (*1993*) reported that GGBS and fly ash can reduce the penetration of concrete by chloride. In order to investigate this further and in relation to this study, chloride tests were carried out on selected mixes. CEM I control and binary mixes were tested at all water cement ratios, together with the 10% limestone ternary at the 55% addition level. At the 35% and 75% GGBS levels, 10% limestone ternary concretes were tested at 0.5 w/c ratio. All tests were carried out at 28, 90 and 180 days. Two different test methods were used, both outlined in Chapter 3. The RCPT is becoming more commonly used but comes under criticism, with regards to the effects of the differing pore solution chemistry and the high voltage (this will be

discussed further later in this chapter). The current passed is related to all, not just chloride, ions in the pore solution and the high voltage applied leads to an increase in temperature especially in low quality concretes. This can, in turn, lead to a further increase in the charges passed. With these criticisms in mind the NordTest (NTBuild 492) was used to support the findings of the ASTM test in this study. The test specimens for both tests are the same size but the preconditioning for the NordTest differs in that following the initial 3 hours vacuuming at a pressure of 10-50 mbar, the dessicator basin is filled with saturated calcium hydroxide de-ionised solution and the vacuum maintained for another hour. The RCPT test required de-ionised/distilled water to completely cover the specimens. Following the preconditioning different concentrations of NaCl were required for each test, 3% by mass for the RCPT and 10% for the NordTest, which measures the chloride penetration depth and a non-steady state migration coefficient, whilst the RCPT data presented the chloride permeability based on charges passed. ASTM C1202 provides a classification scheme for interpretation of the data as given in Table 8.2.

Table 8.3: Chloride permeability based on charge passed (ASTM C1202)

Charge Passed (Coulombs)	*Chloride Permeability*	*Typical of*
>4000	High	High w/c ratio (>0.6) conventional PCC
2000-4000	Moderate	Moderate e/c ratio (0.4-0.5) conventional PCC
1000-2000	Low	Low w/c ratio (<0.4) conventional PCC
100-1000	Very Low	Latex-modified concrete or internally-sealed concrete
<100	Negligible	Polymer-impregnated concrete, Polymer concrete

8.4.1 Rapid Chloride Permeability Tests (ASTMC1202)

As shown in Figure 8.11 at all w/c ratios and ages the binary mixes gave lower values than the CEM I control. Whilst by 180 days the binary mixes indicate low chloride permeability at 0.35 and 0.5 w/c ratio, the CEM I control shows moderate chloride permeability as per the ASTM guidance for these w/c ratios. The increase to 0.65 water cement ratio also gave

expected results for the CEM I control mix. The lower level of GGBS replacement (35%) was a little higher than the other binary mixes, indicating moderate chloride permeability, whilst the other, higher, GGBS level concretes still indicate low chloride permeability' even at this high water/cement ratio.

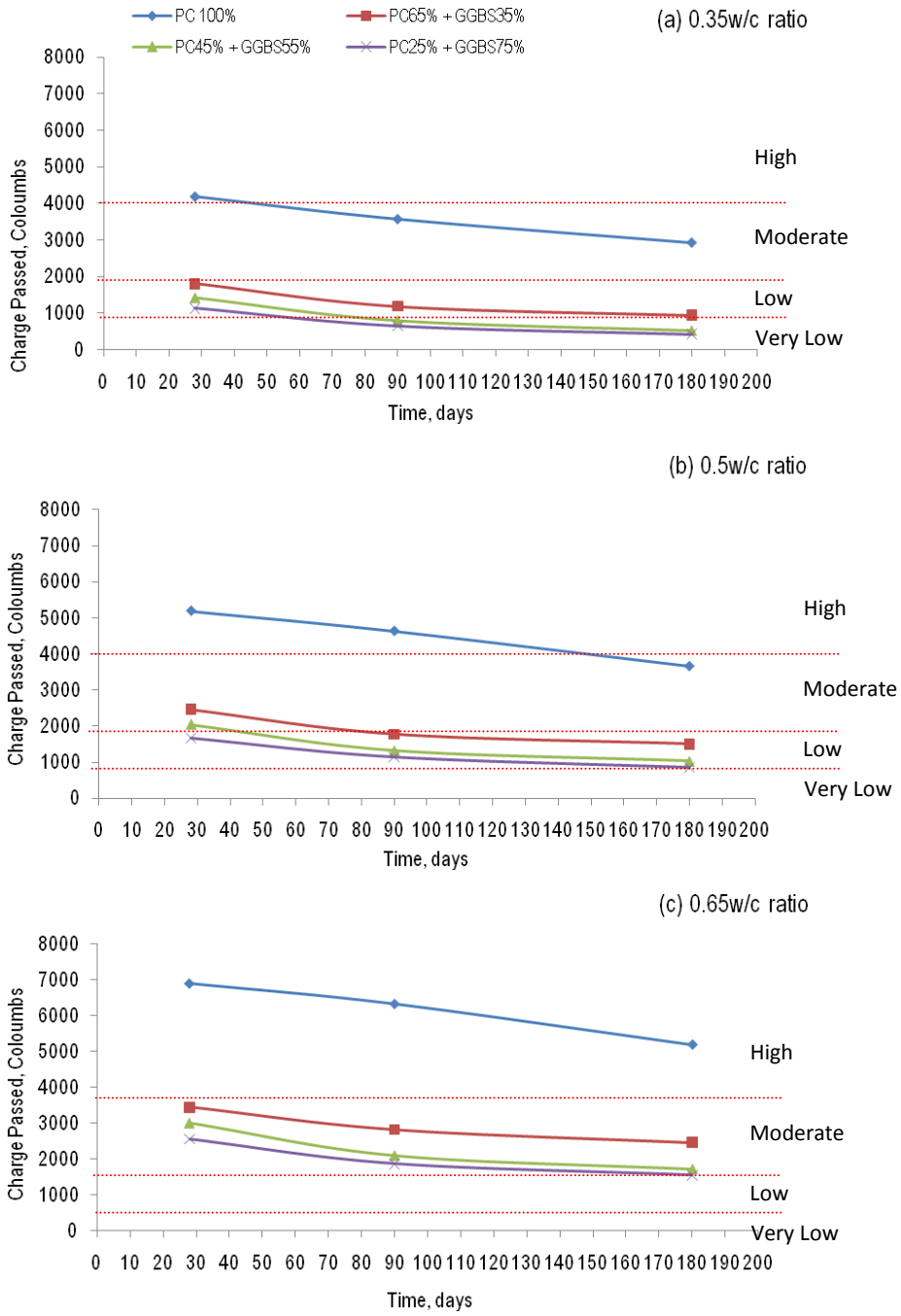


Fig 8.11: Rapid Chloride Permeability Test (RCPT) results for binary mixes for all water cement ratios

Figure 8.12 summarises the data for all binary and limestone ternary concretes at 0.5 w/c ratio that were tested. From the test results it is clear that the CEM I control mix gave high chloride permeability at 28 days and moderate at 180 days. The binary and ternary mixes tested indicate moderate chloride permeability at 28 days and low by 180 days across all w/c ratios tested.

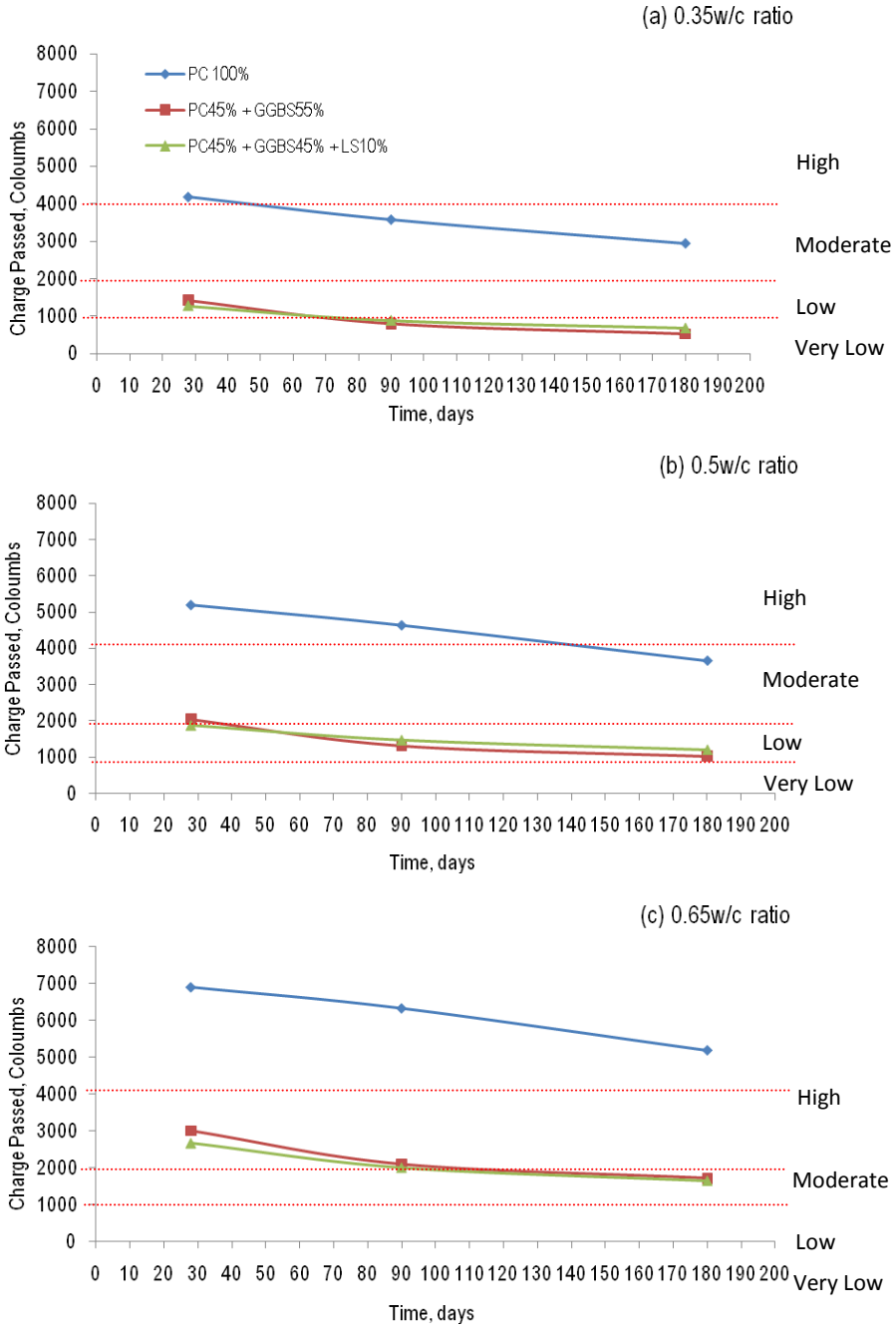


Fig 8.12: Rapid Chloride Permeability Test (RCPT) results for 55% replacement level for all water cement ratios

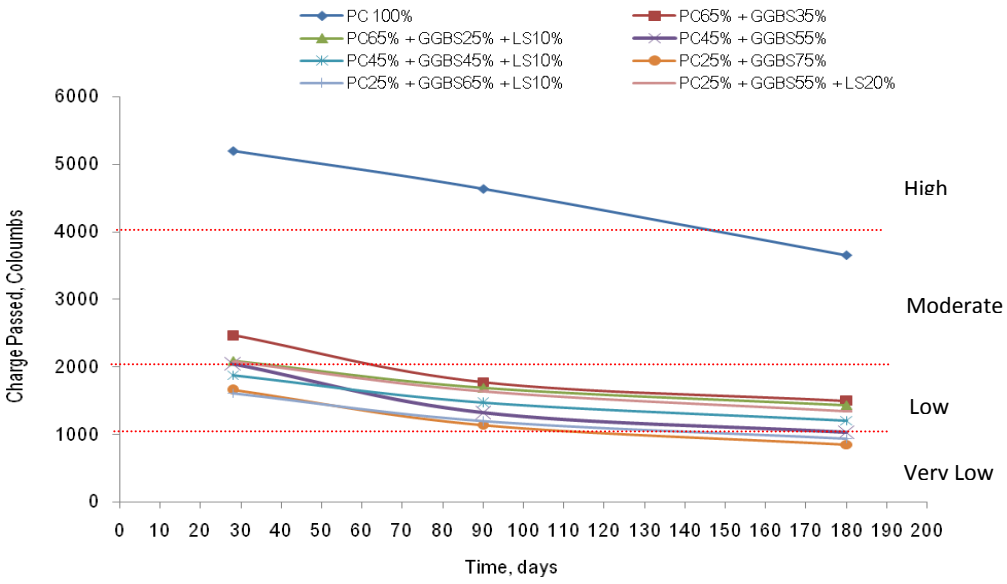


Fig 8.13: Rapid Chloride Permeability Test (RCPT) results at 0.5 water cement ratio

It was suggested earlier that whilst the RCPT test is being more widely used, it has been criticised for example, by both Hale et al (*2002*) and Gowripalan & Mohammed (*1998*). Hale et al (*2002*) stress that caution be used when testing concretes with additions. It is suggested that differing factors can affect the parameters of the test results giving misleading data for three main reasons. Firstly, Sharfuddin Ahmed et al (*2008)* imply that it is an index test in which no steady-state conditions exist and the measurements are taken before this is reached. Secondly the difference in pore solution chemistry of ternary blended concretes may not allow for a true representation of chloride permeation, the current passed is related to all ions within the pore solutions and not just chlorides. Finally, the high voltage used in the test can lead to a temperature rise, increasing the charge passed. In spite of these, however, and mainly due to its convenience and duration the RCPT, as stated earlier, is becoming commonly used. Hale et al (*2002*) used the RCPT and tested a number of blended cements including fly ash and GGBS ternary mixes when showed little effect on the chloride ion penetrability at 28 days and 15-20% reductions compared to other mixes at 90 days.

8.4.2 Non-steady State Chloride Migration (NT Build 492)

The NordTest method produced similar trends in the data to the RCPT tests, but in different terms. Instead of coulombs, the data is expressed as a non-steady-state migration coefficient (D^{nssm}, m^2/s). Figure 8.14 shows that the CEM I concrete again gave higher results, increasing with w/c ratio and the binary concretes were similarly grouped, with the coefficient reducing as the level of GGBS increased and w/c ratio reduced. The inclusion of 10% limestone at the 55% GGBS level is shown in Figure 8.15 and indicates a more noticeable decrease in comparison with the RCPT tests (Figure 8.12). The rate of decline with age was greater for the CEM I control mixes in both sets of tests, but still remained higher than the binary and ternary concretes. The test carried out at 0.5 water/cement ratio, summarised in Figure 8.16, again shows similar results to the RCPT test. The 10% limestone ternary concrete at the 55% level gave the lowest coefficient for the NordTest at 180 days, compared to the RCPT tests which indicate that the binary mix at this level was only marginally lower, but the 75% GGBS level binary concrete gave the lowest results for the RCPT, as indicated earlier in Figure 8.13.

It was evident from the data that an increase in addition level had a positive effect in reducing chloride ingress. It therefore appears that CEM I is the component within the concrete that has the most negative effect on the durability in this instance. The addition of GGBS to the CEM I had a combined effect, not only in creating a denser microstructure but reducing the level of calcium hydroxide (*Hooton & Titherington, 2004*). A positive dilution effect was seen throughout the tests. As the volume of addition increased, the resistance to chloride ingress improved. As with all previously reported tests, the w/c ratio had a noticeable effect on chloride ingress, though for the combination mixes it remained moderate or low. Interestingly, the limestone additions had the result of reducing chloride ingress at the earlier test age. This corroborates Hornain et al's (*1995*) findings which attribute this to the filler effect on the tortuosity of concrete. 10% limestone appeared to be the optimum level as an increase to 20% showed a rise in chloride penetration, although it still remained lower than the CEM I control mix. These findings are in line with those of Ghrici et al (*2007*) whose study found that an increase in limestone to 15% increased chloride penetration, agreeing with Bonavetti et al's earlier study in 2000.

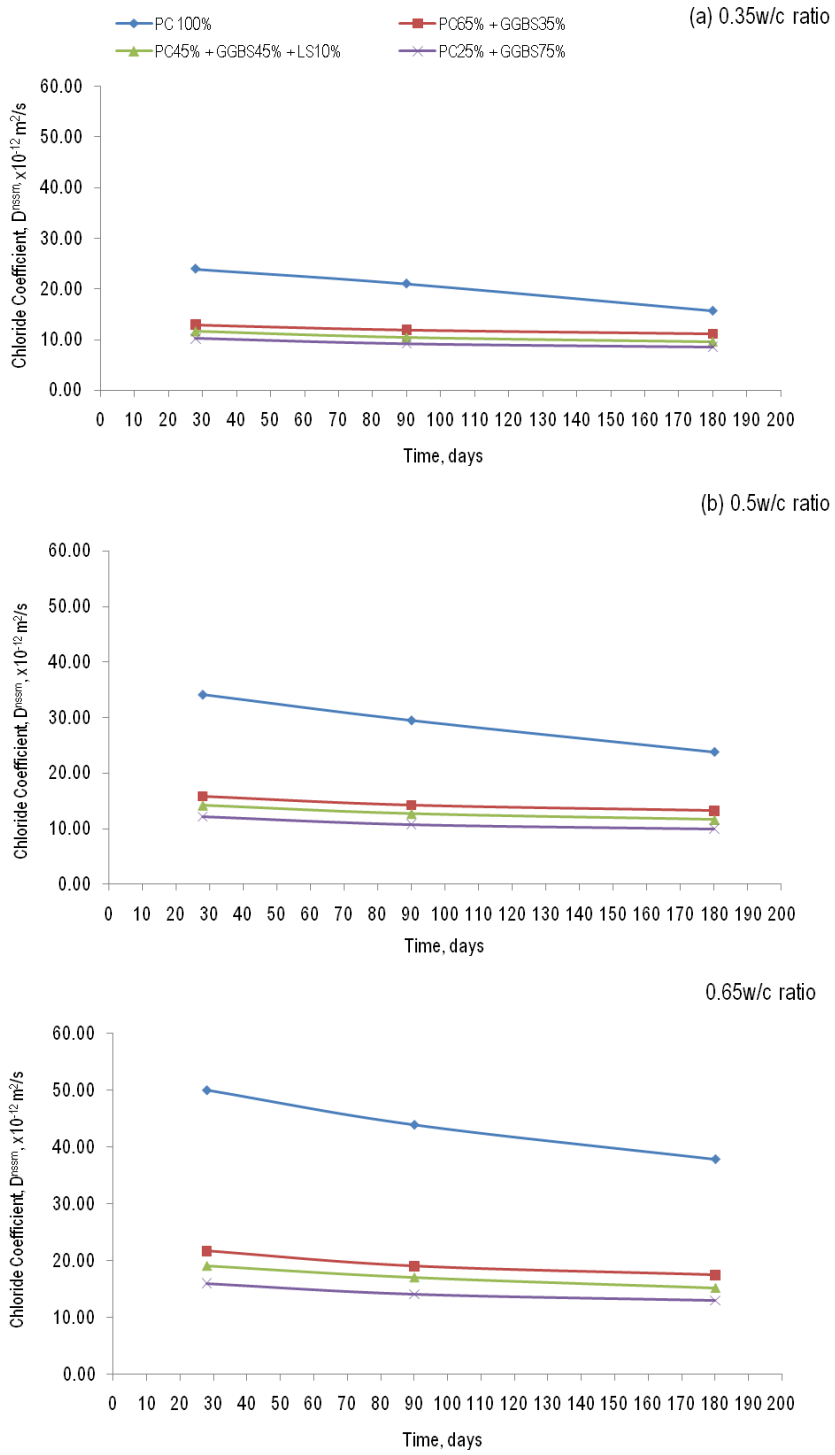


Fig 8.14: Non-steady state chloride migration, (NT BUILD-492) results for mixes for all w/c ratios

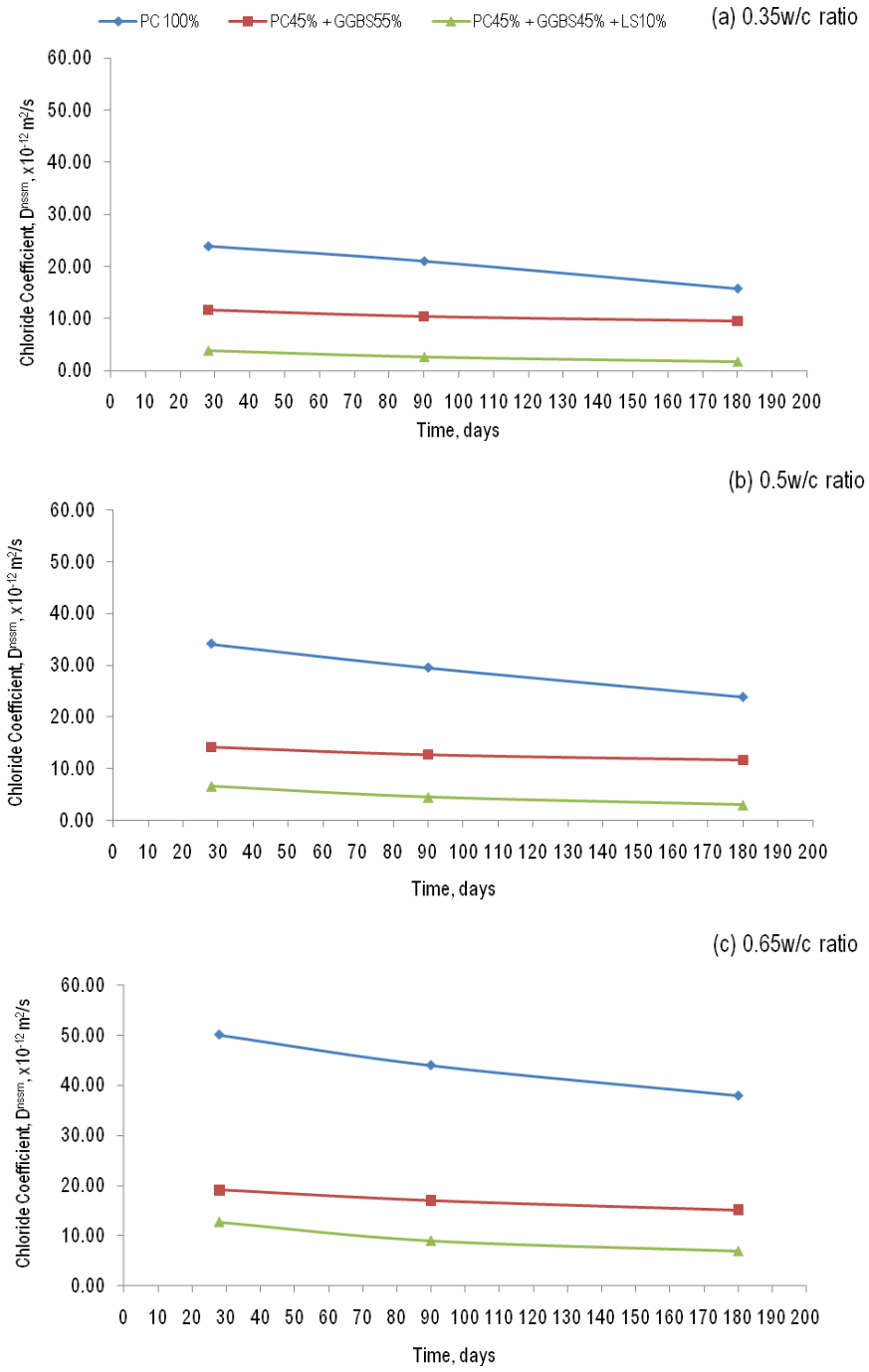


Fig 8.15: Non-steady state chloride migration, (NT BUILD-492) results 55% replacement level

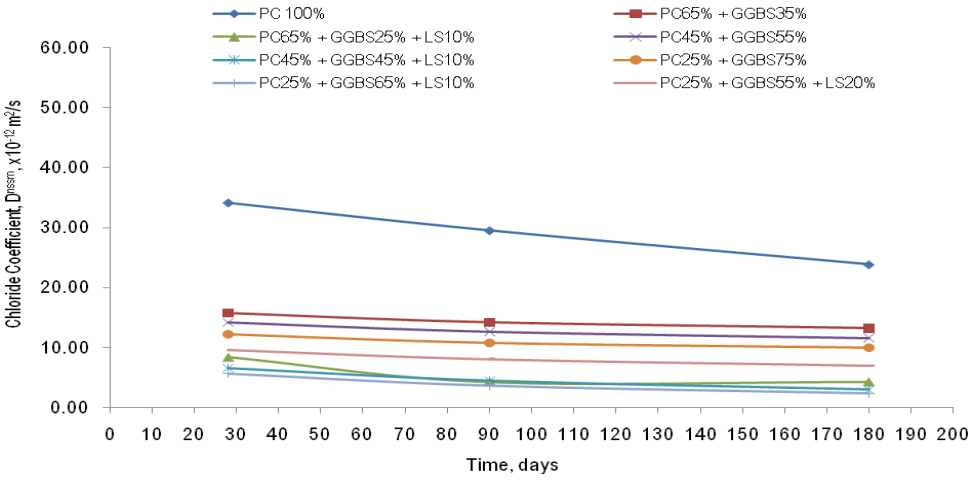


Fig 8.16: Non-steady state chloride migration, (NT BUILD-492) results at 0.5 water cement ratio

Table 8.4: Summary of Chloride Ingress Results

Concrete Type	W/C Ratio	NON-STEADY STATERAPID CHLORIDE MIGRATION, NT BUILD-492			RAPID CHLORIDE PERMEABILITY, ASTM		
		Dnssm, x10^{-12}m^2/s			CHARGE PASSED, COLOUMBS		
		28	*90*	*180*	*28*	*90*	*180*
CEM I 100%	0.35	23.95	21.04	15.70	4181	3574	2935
CEM I 100%	0.50	34.12	29.52	23.86	5195	4635	3655
CEM I 100%	0.65	50.07	43.97	37.90	6905	6335	5200
CEM I 65% + GGBS35%	0.35	12.95	11.91	11.12	1800	1185	945
CEM I 65% + GGBS35%	0.50	15.80	14.22	13.23	2465	1775	1500
CEM I 65% + GGBS35%	0.65	21.65	19.00	17.45	3445	2825	2465
CEM I 65% + GGBS25% + LS10%	0.50	8.41	14.29	4.33	2085	1690	1435
CEM I 45% + GGBS55%	0.35	11.60	10.41	9.55	1425	800	525
CEM I 45% + GGBS55%	0.50	14.20	12.68	11.62	2045	1322	1030
CEM I 45% + GGBS55%	0.65	19.10	17.03	15.15	3005	2100	1720
CEM I 45% + GGBS45% + LS10%	0.35	3.81	2.59	1.65	1275	885	680
CEM I 45% + GGBS45% + LS10%	0.50	6.56	4.47	2.99	1878	1474	1205
CEM I 45% + GGBS45% + LS10%	0.65	12.76	9.05	6.99	2685	2015	1655
CEM I 25% + GGBS75%	0.35	10.21	9.22	8.60	1130	650	425
CEM I 25% + GGBS75%	0.50	12.21	10.81	10.02	1665	1140	850
CEM I 25% + GGBS75%	0.65	16.00	14.08	12.96	2555	1870	1550
CEM I 25% + GGBS65% + LS10%	0.50	5.65	3.62	2.32	1605	1195	935
CEM I 25% + GGBS55% + LS20%	0.50	9.65	8.11	7.03	2080	1640	1345

8.5 Correlation Between Chloride Tests and other Concrete Properties

8.5.1 RCPT and NordTest

As with previous test data correlation between tests was determined by using statistical techniques to indicate if selected pairs of data, or variables, relate to each other. An R^2 value is obtained ranging from +1 to -1, showing a positive or negative relationship respectively. A correlation coefficient of >0.80 shows the existence of a relationship between two variables in different units (*Salkind, 2000*).

Both tests were compared against each other and are shown in Figure 8.17. It can be seen that at the lower test ages there was a strong correlation between both sets of test data across all 3 w/c ratios. By 180 days, however, the strongest correlation was seen between the higher 0.65 w/c ratio. At this age, the concrete has matured and little further hydration takes place within the concrete structure.

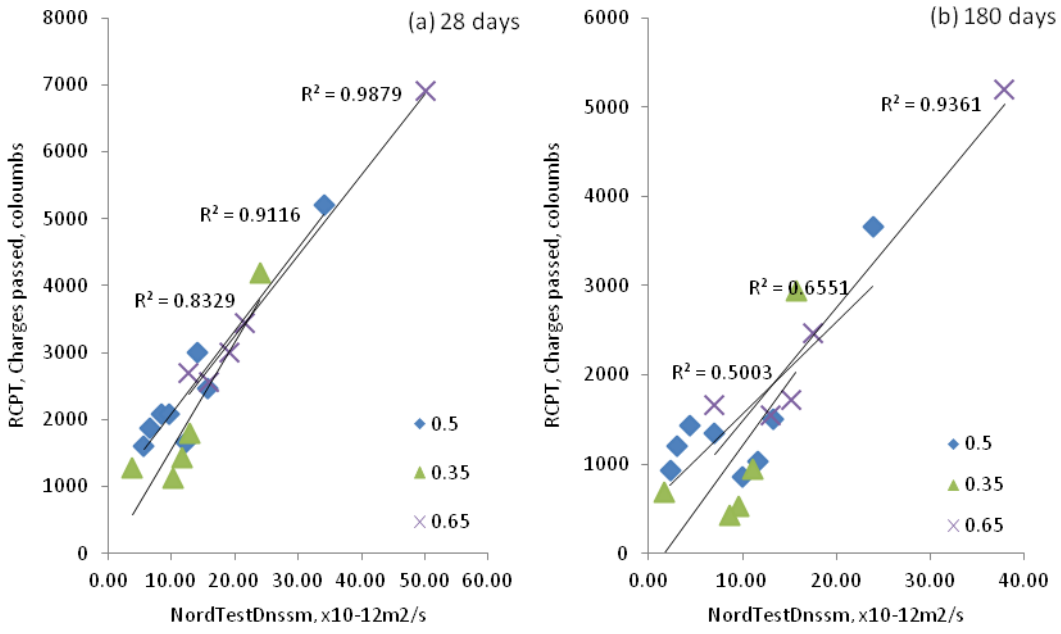


Fig 8.17: Correlation between RCPT and NordTest

8.5.2 Chloride Ingress and Porosity

As with previous data analysis the chloride results were examined in relation to porosity and critical pore size. Figures 8.18 to 8.21 illustrate the generally low correlation that exists between these properties. A better correlation is seen in Figure 8.18 between the critical pore size and the NordTest for the 0.35 w/c ratio at 180 days. The pore correlation seen between these properties are indicative of the complicated and multi-mechanism phenomenon of the transport of chloride ions into concrete.

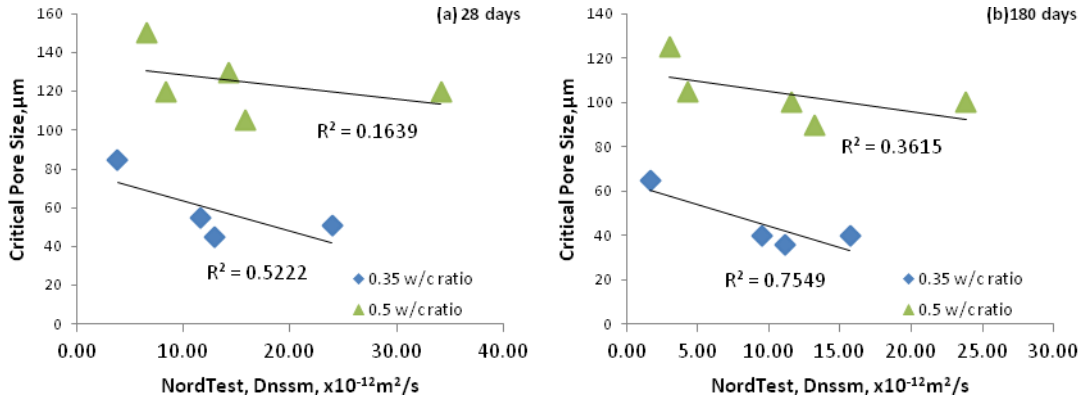


Fig 8.18: Critical pore size against NordTest

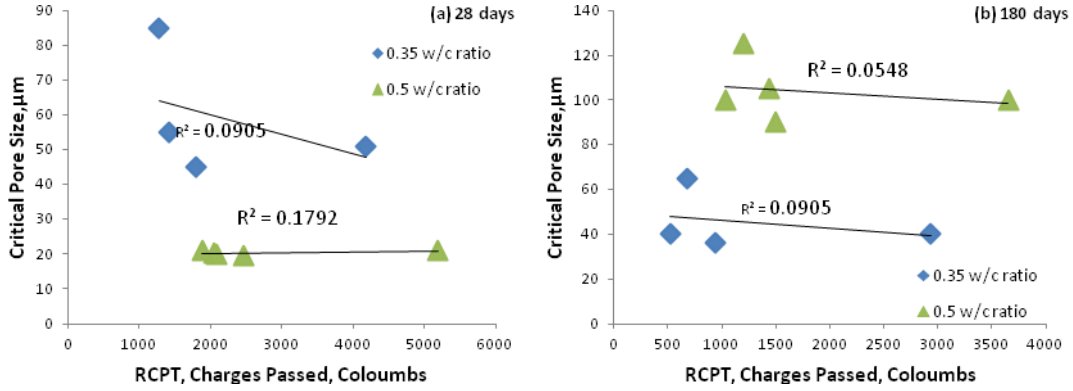


Fig 8.19: Critical pore size against RCPT

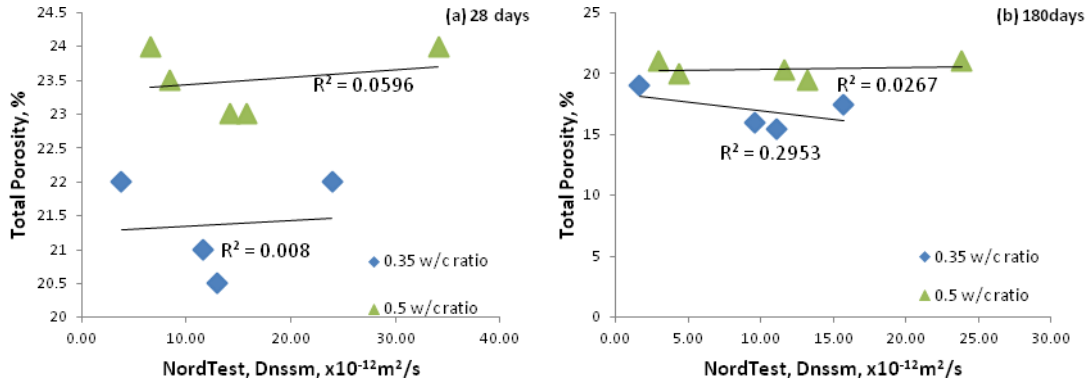


Fig 8.20: Total porosity against NordTest

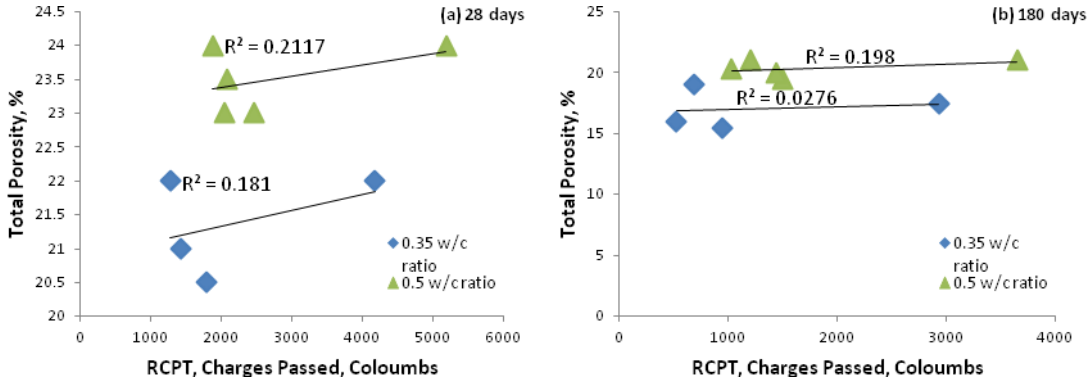


Fig 8.21: Total porosity against RCPT

8.5.3 Chloride Ingress in relation to other properties tested

The data from both chloride tests is plotted in relation to the other concrete properties tested in order to ascertain if any correlation exists. Figure 8.22 shows this data at 28 days and clearly indicates that little if any correlation can be found between chloride ingress and (a) ISAT, (b) intrinsic air permeability and (c) water penetration. The poor correlation seen between these properties are indicative of the complicated and multi-mechanism phenomenon of the transport of chloride ions into concrete.

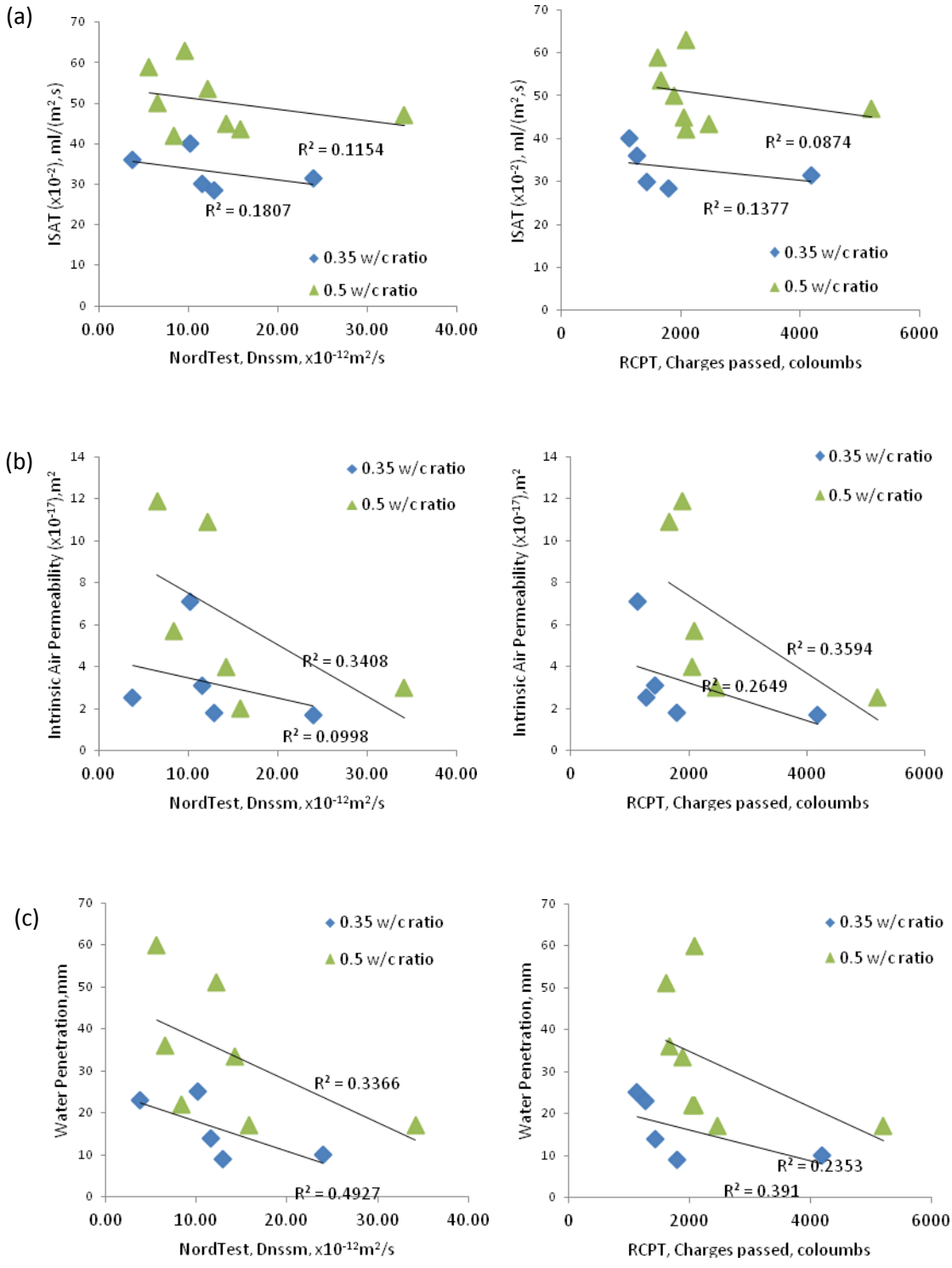


Fig 8.22: Correlation between Chloride ingress tests and other tested concrete properties (a) ISAT; (b) Intrinsic air permeability; (c) Water penetration

8.6 Chloride Binding

It was alluded to earlier that regardless of the transportation process of chloride, it will be affected by the pore structure and interaction of ions within the pore solution with the pore walls by way of chloride binding and membrane effects. The latter involves the production of ion exchange membranes by the surface charge on the pore walls that is balanced by equal and opposite charges in the pore solution. Whilst both chloride tests discussed, measured the transportation of chloride due to the conductivity of concrete, they neglect the chloride interaction with the solid phase. Papadakis & Tsimas (*2002*) state that this is an important process, specifically chloride binding during the reaction process, as it is key to the resistance of chlorides. This was later confirmed by Glass et al (*2008*) who stated that chloride binding capacity is a function of the relationship existing between the total, free and bound chloride in concrete.

The chloride binding within concrete is dominated by the reaction of C_3A to produce calcium chloroaluminate, generally referred to as Freidel's salt ($3CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}10H_2O$). The Freidel's salt plays a key role in 'locking up' chloride ions within the concrete structure. In this sense, it may be considered that a high C_3A content will therefore affect the chloride binding in a positive manner.

$$3Ca \cdot Al_2 \cdot CaCl_2 \cdot 10H_2O \leftrightarrow 4Ca^{2+} + "Al(OH)_4 + 2Cl + 4OH + 4H_2O$$

[Eq 8.5]

However, other reactions need to be taken into consideration. In addition to being chemically bound, chloride ions can also be physically absorbed by C-S-H gel. Given that GGBS produces more C-S-H gel during hydration than CEM I, this is likely to contribute to reduction of chloride ingress. It is therefore evident that both GGBS and fly ash can affect the rate of binding of chlorides (*Glass & Buenfeld, 2000*). There is also the possibility that capillary pores formed during early hydration can be blocked by further hydration products during the curing of the concrete if there are sufficient hydration products produced as the concrete matures. Pore blocking is likely given the increased production of CSH by the binary and ternary contents and the wet conditions of the test.

The composition of cement, as already alluded to, is the most influential factor affecting chloride binding. Whilst the C_3A affects the amount of AFm phase, alumina ferric oxide, monosulfate phase that forms *inter alia*, when tricalcium aluminate reacts with dissolved calcium sulfate. In addition to the C_3A, C_3S and C_2S can be correlated with the amount of CSH formed upon hydration. The presence of alumina (Al_2O_3) is also a precursor to increasing chloride binding capacities and with GGBS having almost three times Al_2O_3 than CEM I (as shown in Table 3.1, Chapter 3) the increase in chloride binding is predictable. The fly ash also has an increased Al_2O_3 content; its effects may be less noticeable given its lower volume by mass in the mix combination.

Although CEM I had a higher content of both C_3A and C_4AF, suggesting that it would result in better chloride binding, the hydration process of CEM I also releases alkalis into the pore solution that can have the effect of reducing internal chloride binding and increases the alkalinity of the sulfates (*Luo et al, 2003*). In contrast, GGBS and fly ash will, due to their low alkali content, incorporate more alkalis into the reaction process than will be released into the pore solution (*Duchesne & Berube, 1994)*. In addition, the higher sulfate content of CEM I will also reduce chloride binding as there is a preferential reaction between C_3A and sulfates. Due to the lower sulfate content of GGBS, the C_3A that is available is free to bind with chloride to produce more Freidel's salt (*Luo et al, 2003*).

With regard to the aggregate content of concrete, there is normally very little effect on the ingress of chloride or chloride binding within the concrete structure. Though Hobbs (*1999*) states that a more permeable aggregate will affect this, in this case the aggregates used in this study were of low absorption and hence not an issue here, nor were the limestone aggregates that may have resulted in the release of additional chloride ions into the pore solution (*Grattan-Bellew, 1996*). With this in mind it is therefore likely that the limestone addition to the cement matrix may result in the increasing chloride ions. This is discussed by Ghrici et al (*2007*) who found that over time limestone concretes will have lower resistivity to chloride ingress than GGBS or fly ash concretes, but still lower than CEM I concrete. The RCPT indicates a slight increase in the longer-term results for the limestone ternary concretes, but the increase was minor. Andrade (*1993*) suggest this increase is due to the higher level of OH^- ions in the pore

solution, acting as a supporting electrolyte. Bonavetti et al (*2000*) also found similar results when testing limestone binary mixes, so it would appear that as a ternary addition this effect is minimised by the reaction of GGBS.

8.5 Summary

With the design service life of the majority of concrete structures exceeding 30 years and given the range of exposure conditions, it is obviously important for concretes to have adequate structural properties and to be durable. Concretes need to be able to withstand corrosion and chemical attack and it became evident from the data that cement additions have a significant effect on the overall durability of concrete.

Depth of carbonation increased with GGBS level and also w/c ratio. Although it also increased with time, the lower level binary concretes were comparable with the CEM I concretes at 20 weeks and for all w/c ratios. The increased depth of carbonation was due to the limited content of calcium hydroxide (CH) resulting in the CO_2 not becoming fixed near the surface of the concrete.

The addition of fly ash did not improve the depth of carbonation, rather it increased it further with increasing levels of addition, from 10% to 20%, and w/c ratio across the range of GGBS levels. This was due to the competition created between GGBS and fly ash and also the limited volume of Ca(OH)2. The limestone concretes also increased the depth of carbonation over the range of mixes, predominantly due to the diluting effect.

Correlation between carbonation and compressive strength was found with a higher depth of penetration noted at lower strength. Similarly it was seen that with higher air permeability increased carbonation occurred and this could be related to critical pore diameter.

In spite of the poor carbonation results, the chloride tests produced much more favourable data showing that the inclusion of binary and ternary additions significantly

improved the resistance to chloride ingress due to their ability to increase chloride binding and in turn the production of Freidel's salts. The was as a result of their overall lower sulfate content and the fact that as a result of hydration GGBS concretes can produce more C-S-H than CEM I.

CHAPTER NINE: ENVIRONMENTAL & ECONOMIC IMPLICATIONS OF ADOPTING TERNARY CONCRETES IN CONSTRUCTION PRACTICE

9.1 Introduction

Thus far the tests carried out on the properties of the concrete combinations have been discussed purely in isolation from an environmental and economic perspective. Whilst each test is fundamental in discovering the strength and durability of blended cements it would be prudent to review the data from all tests carried out in a laboratory setting and to try and understand their value in an industrial context and the implications of using such concretes in modern society which involves the economics of an ever increasing industry that more recently has had to review their own impact of the global environment.

It goes without saying that historically cement, or concrete, has played a significant role in the construction industry for many millennia. Ancient Egyptians, Romans and Greeks have built fantastic structures, some that remain to this day as a testament not only to these civilisations' architectural prowess but to the strength and durability of the material itself. However, modern society brings contemporary pressures on the concrete industry in a growing global market. The call for the use of more environmentally, or sustainable, materials is increasing as external pressure is placed on a global industry and whilst European standards such as BS EN 197 permits the use of constituent materials, it is limiting their properties and amounts. The use of additions is also covered in BS EN 206 and BS 8500 but a lack of understanding is limiting and needs to be addressed before further headway is made into the greater use of materials such as GGBS and fly ash as no trade off can be afforded between the strength and durability of concrete and the environment.

9.2 Life Cycle Analysis

The benefits of using binary and ternary cements can be threefold with financial and environmental remuneration, as well as improved technical performance but at present minimum cement concrete specifications can inhibit the opportunity to move towards a change more ardently. Whilst demands are constantly being made on industry to reduce environmental impact and lean towards sustainable practices there are, without a doubt, cost implications of complying with environmental standards. It is, after all, an industry driven by market conditions. As with any other industry there are a number of issues that need to be addressed with regard to cement's impact throughout each stage of its lifecycle, from its production to demolition. Life cycle analysis is a widely used method within the construction industry (*Hambert, 2012; Ortiz et al,2008*) and is based on ISO 14040 (*ISO, 2006*). Figure 9.1 illustrates in basic terms the lifecycle of concrete as well as providing an overview of the complexities of just one element, the production of cement.

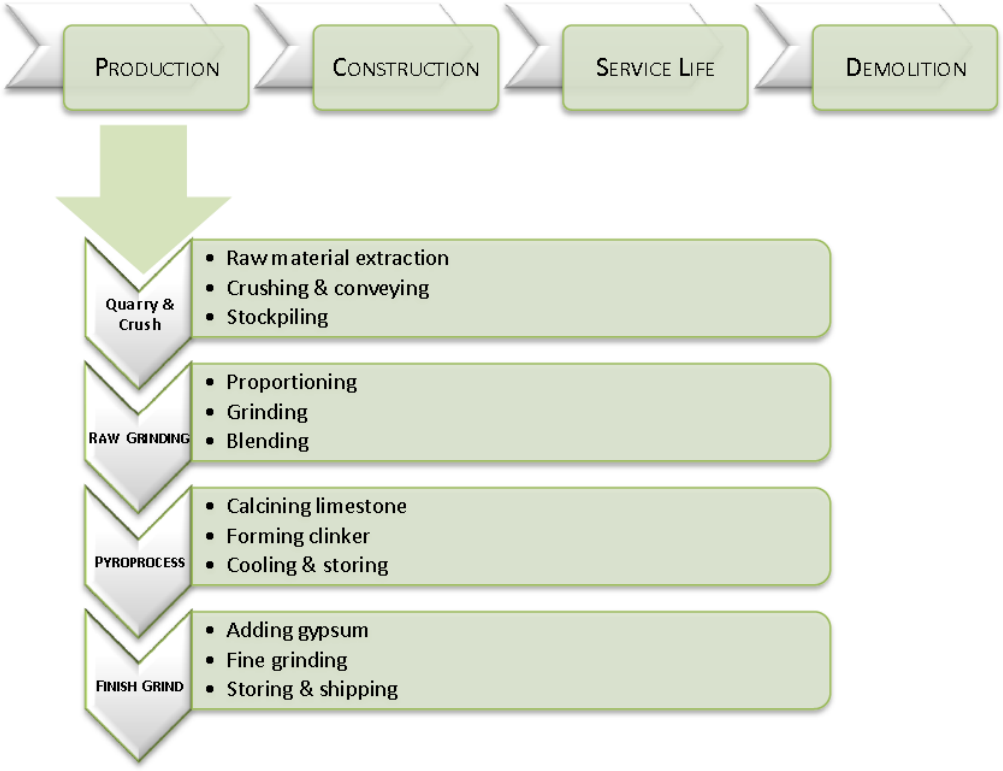


Fig 9.1: Lifecycle of concrete

Vast quantities of materials and energy are required throughout the production, construction and service life of a building that will be affected by, not only its design but by the selection of materials that can have beneficial thermal properties to aid reductions in energy use. Significantly, yet often disregarded, are the cultural and market forces that can affect the service life of a building that may have to be adaptable and change function several times throughout its life, requiring renovation and repair, though the later can be abated to some extent by the use of durable materials. It is evident from Figure 9.1 that there are a number of influential factors and to examine the complete lifecycle, inputs and outputs from each element in detail, would be exhaustive and can lead to further complications when considering the use of additions such as GGBS and fly ash. In order to undertake an accurate analysis it may be argued that these additions need to be incorporated into a complete system boundary as illustrated in Figure 9.2, (taken from Hambert, 2012) given that their own production results in CO2 emissions. This may be disputed if they were to be considered as a waste product but under EU directives they are to be regarded as by-products due to meeting the following criteria (*EU, 2008*):

1. further use of them is certain;
2. they are produced as an integral part of a production process;
3. they can be used directly without any further processing other than normal industrial practice;
4. further use is lawful.

Previously, no environmental burdens, other than disposal, were placed on waste as it is unintentionally produced. However, with GGBS and fly ash, meeting these four criteria their impact now needs to be given more consideration in terms of the allocation of environmental burdens and the partitioning between both the main product and the by-product (*Chen et al, 2010*). This can be done by one of two ways; mass ratio allocation and economic ratio allocation, both can lead to less favourable outcomes and greater environmental impacts when GGBS is compared to CEM I. Figure 9.3 (from *Chen et al, 2010*) illustrates this point when a mass of GGBS (1.11kg) equivalent to the replacement of 1kg of CEM I is compared. The same is shown for fly ash in Figure 9.4.

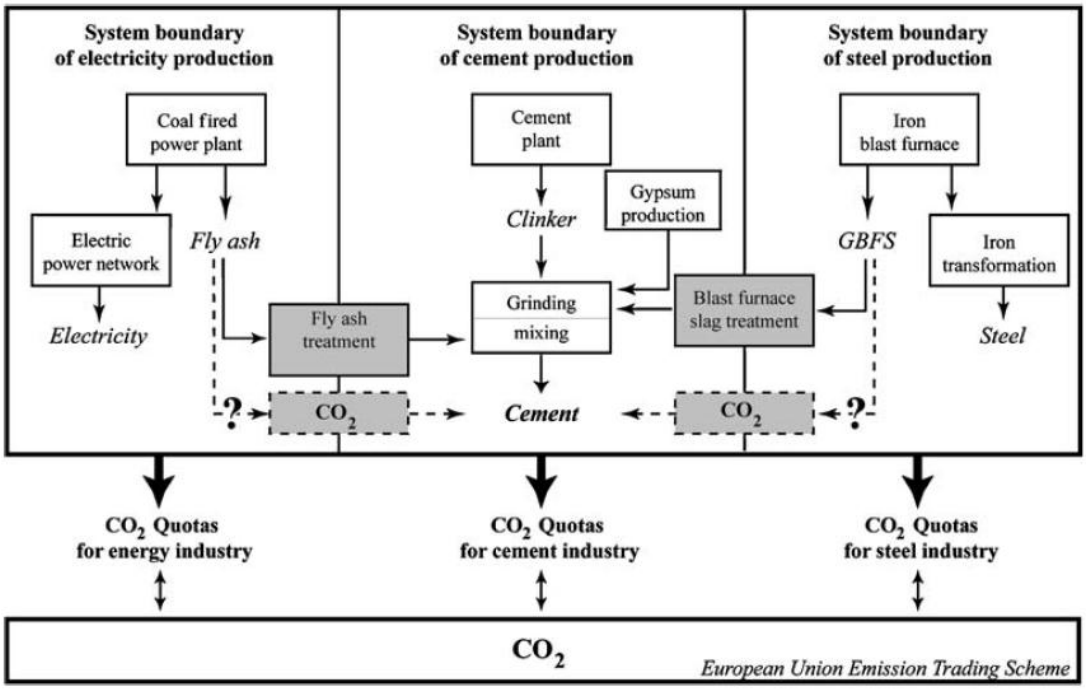


Fig: 9.2: System boundaries of cement production

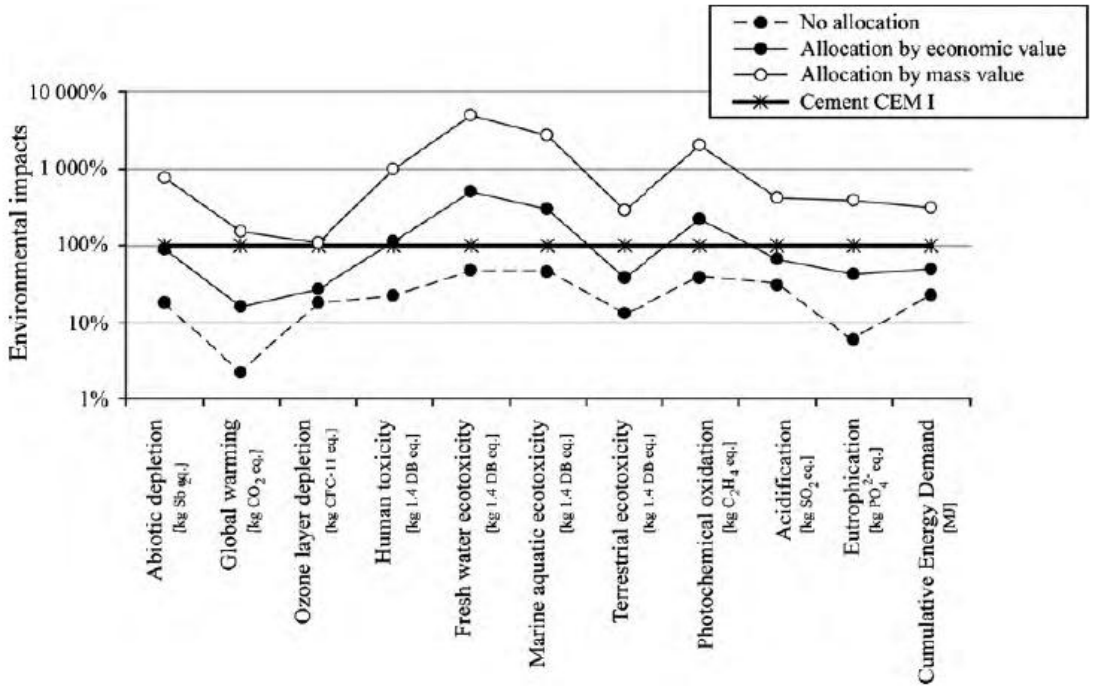


Fig 9.3: Environmental impact of GGBS

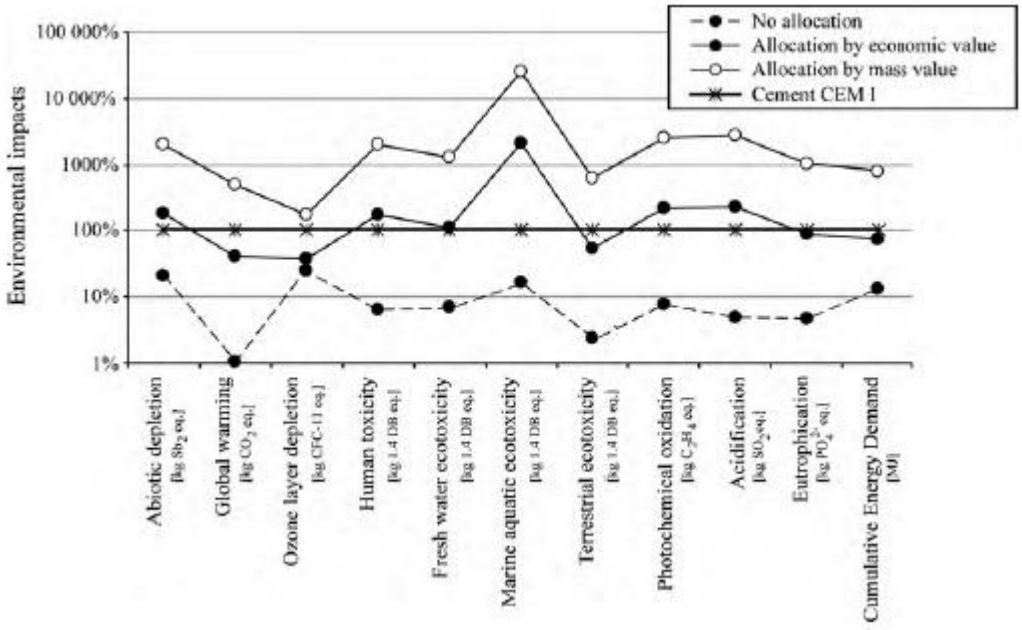


Fig 9.4: Environmental impact of fly ash

It is evident that there are a number of elements to the production of GGBS that would also need to be considered when examining the life cycle assessment of cement if a holistic and all-encompassing approach was to be taken. There still remains some contention as to which method of allocation is more indicative of the environmental impact of GGBS, and indeed fly ash, as an addition to cement. Mass ratio allocation clearly results in a negative outcome, on face value, for both GGBS and fly ash and whilst economic ratio allocation is shown more favourably, given its advantage in lowering the environmental impact, it is unclear as to whether the environmental burden has proportioned fairly. Essentially GGBS and fly ash are by-products of primary industries, as defined by the 2008 Directive, but if they had no positive value to the cement industry, in that they can potentially enhance the strength and durability properties of concrete, they would be waste and should, therefore, not be given the same allocation as the main products. This issue is discussed by Chen et al (*2010*) who also stated that economic ratio allocation can fluctuate due to market prices.

Given the uncertainty of both mass ratio and economic ratio allocation a third option can be considered; that of non-allocation. GGBS and fly ash are regarded as waste and as such no allocation of environmental burden is proportioned, this method has been adopted by both

Flower & Sanjayan (*2007*) and Xing et al (*2008*). Undeniably this area would benefit from a separate and extensive study. However, this chapter will focus simply on the embodied ECO_2 of the blended concretes and relate it to the concrete properties tested and attempt to show possible material cost implications to illustrate the potential for blended concretes industry wide. Given the current economic climate costs can be influential and a deciding component in choosing the materials used. Cheaper poorer quality cement may be selected over more durable if standards were not in place in Europe but the use of additions such as GGBS or fly ash may be able to bring costs down in both an economic and environmental sense.

9.3 Environmental Impact

As discussed previously and in Chapter 2, there are a number of issues facing the concrete industry that need to be addressed concerning its environmental impact. With 5% of global anthropogenic CO_2 emissions being caused by the production of cement (*Hendricks, 2005*) it is not just resource management by way of raw materials and energy that needs to be considered by industry. The production of cement is in itself, an energy intensive process with 2% of global primary energy consumption used (*WEC, 1995*), with 1.75± 0.1 MJ needed for each kg of clinker produced (*Taylor, 1992*) and can range in ratio with cement depending on the quality, from 0.5 to 0.95 depending on the type of cement used, the latter for Portland cement.

The CO_2 emissions emanate from both the combustion and calcinations process with 0.5 tonne of CO_2 emitted for every tonne of CaO produced as part of the following chemical reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$

[Eq 9.1]

As discussed in Chapter 2, this decomposition of limestone is an essential part of cement production and occurs within the kiln which, also consumes high levels of energy creating further CO_2 emissions. However, as suggested by *Damenili et al* (2010) there are consolidated strategies to reduce CO_2 emissions supporting *Hendricks* earlier views (2005). Essentially increasing the energy efficiency of kilns or the use of alternative fuels involves

extensive capital outlay for producers. The substitution of clinker by mineral additions such as GGBS, to improve the efficiency of cement use and thus formulate more eco efficient based products is by far a more economically attractive option. The use of blended cements depends very much on current application levels, availability, standards and legislation in terms of affecting market conditions. Standards already restrict the quantity of additions used in blended cements, depending on a number of factors such as strength requirements and exposure conditions as discussed in Chapter 2 and indicated in Table 2.6, extracted from BS EN 197-1.

9.3.1 Embodied CO_2 (ECO_2)

The use of binary concretes is increasing with a number of global case studies as discussed in Chapter 1, such as the QE2 Bridge, Dartford and the Meridian Energy Building, Wellington New Zealand. The availability of materials such as GGBS is limited and continues to be stretched due to less manufacturing of pig iron, again another result of recession (*Higgins, 2011*). Fly ash is in good supply, but it is not limitless and some move towards the use of other, ternary additions, needs to be encouraged to not only mitigate the shortfalls of GGBS and fly ash (for example resistance to carbonation) but to reduce the strain on supplies. In order for application levels to change standards and legislation need to evolve to permit greater use of these ternary materials but this cannot occur without the continued studies into the effects they have on the strength and durability of concrete. The tests carried out and discussed previously will be shown in relation to their calculated ECO_2 in light of the growing pressures on the concrete industry to be more sustainable.

In order to calculate more accurately the ECO_2 of the mix combinations other components must be considered. Typical proportions of the components of concrete are shown in Table 9.1. The ECO_2 of cement has already been discussed and given the amount required to produce 1 tonne of concrete the ECO_2 is high when compared to that of the sand and aggregates. The production process of sand and fine aggregates involves hauling, washing and grading requiring equal amounts of diesel and electricity. Flower & Sanjayan (2007) report on audit findings for one quarry in Australia where the ECO_2 is said to be in the region of 0.0139 t CO2 –e/tonne and includes the subsequent transportation of the sand to the mixing site. The

production process of coarse or crushed aggregate is generally 30-40% higher in emissions than that of sand depending on the type of aggregate being used. The process itself begins with blasting from quarry faces into medium sized rocks before excavating and hauling to crushing and grading equipment. Flower & Sanjayan report the ECO_2 for basalt to be 0.046 t CO2 – e/tonne. The process also requires on average 22% diesel and 78% electricity, the latter of which is used extensively for the crushing stage which itself accounts for 75% of the total process. The Concrete Industry Sustainability Performance Report, published in 2010, indicates the CO_2 emissions per tonne of aggregate produced to be 4kg per tonne, not differing greatly from Flower & Sanjayan. Table 9.1 summarises the proportions, energy use and ECO_2 of each component, where given, making 1 tonne of concrete.

The emission figures are based purely on the processing of materials subsequent to their initial production as both GGBS and fly ash are by products of other industrial processes that operate independently of the cement industry and would therefore be produced regardless of their beneficial characteristics as cement additions. Use of these materials in cement production has the added benefit of reducing waste to landfill in addition to that of reducing ECO_2 per tonne of concrete produced.

Table 9.1: Proportional components of 1 tonne of concrete

	Proportion	Energy (kWh/t)*	Water (l/t)*	ECO_2
Cement	12%	1194	45	70-100%
Aggregate	48%	12.7	48	4-6%
Sand	34%			1%
GGBS		238	11	5.2%
Fly ash		9.3	0	0.4%
Limestone				3.2%
Water	6%			

*used in production/processing of materials

With the information summarised in Table 9.1 the ECO_2 of all concrete combinations was calculated for each kg/m^3 of concrete produced. The data is shown in Appendix A-4 whilst Figure 9.2 shows an overview of the ECO_2 values for each mix across the range of w/c ratios.

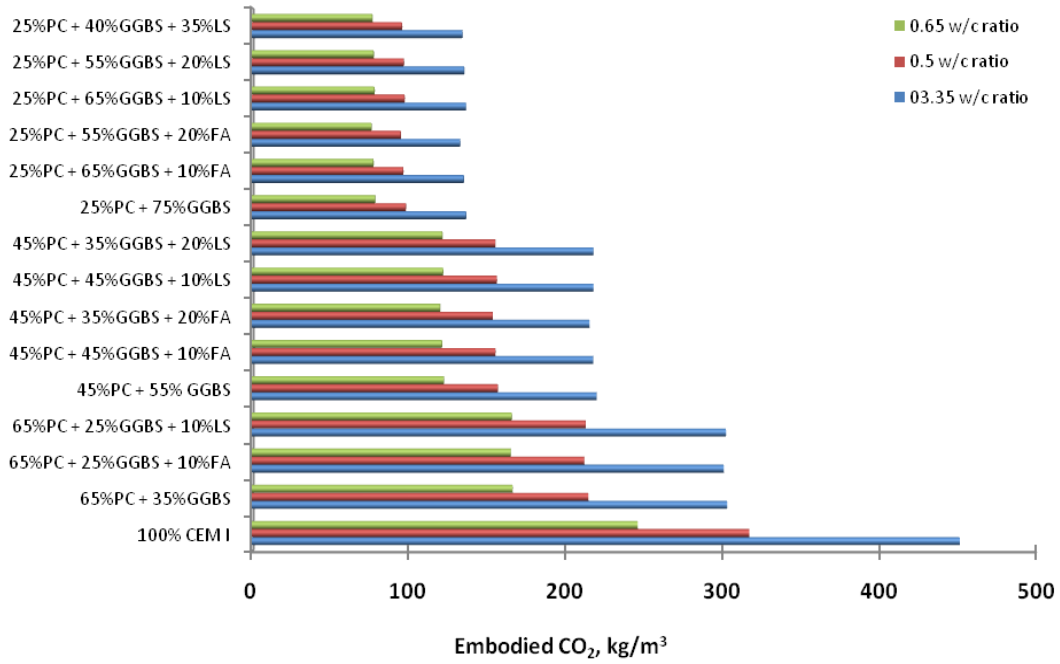


Fig 9.2: Calculated ECO_2 for all mix combinations and w/c ratios

9.4 Environmental Performance

9.4.1 Strength and ECO_2 Trade-off

In Chapter 4 the early age strength and the estimated time to reach 10N/mm^2 was discussed. Given the delayed strength development properties of the additions it is expected that CEM I will reach 10N/mm^2 earlier, but as shown in Figure 9.2 the ECO_2 of the CEM I mix is higher than the others. However, whilst it is important to ascertain the strength of concrete, in general laboratory testing cannot provide a true representation of the environmental effects that in situ concrete may endure; such tests do not accurately reflect the strength development of in situ concrete that is affected by a number of variables such as thickness of slab, binder content and temperature.

Given the extent and diversity of concrete as a building material its strength remains an important, if not vital, statistic in selecting the right type of concrete for the right construction project. Formwork is extensively used, creating further restrictions on the management of these projects. BS 8110 (1997) and subsequently CIRIA Report 136 (2004) lay out guidelines for the striking of formwork. Four days is recommended for the soffit formwork to slabs and 12hrs for vertical formwork at an ambient temperature of 16^{o}C. Shorter periods are acceptable for slabs and beams only if their strength is equal or greater to 10 N/mm^2 in situ, or twice the stress to which they are being subjected (10 N/mm^2 is usually the greater of these) 5N/mm^2 is acceptable for members in compression to protect against frost damage. Should, however the slab be less than 250mm in depth and have a length of at least 7.5m shorter periods are not allowable. With this is mind it is evident that all mixes for 0.35 and 0.5 w/c ratio were suitable when the time to 10N/mm^2 is assumed to follow a logarithmic scale as is suggested by Li & Zhao (2002). It must be remembered that this is hypothetical in this instance and the time to 10N/mm^2 is assumed based on the early strength development from test data and may not necessarily be the case. However, regardless of these assumptions, the result for 3 days exceeded 10N/mm^2 for all these mixes and therefore definitely conformed to the 4 day restriction. It may be possible that early strength development of concrete does not follow a logarithmic scale but gives a rapid growth during the initial 24 hours, further tests would need to be carried out in a spate study, which would be needed to take place to confirm this before a decision is made as to the best combination for vertical formwork requiring 12 hours to reach 10N/mm^2.

The British standard recommendations are irrespective of binder type and a later report produced by CIRIA (CIRIA Report 136, 1995) provides tables for CEM I strength classes 42.5 and 52.5 only without due consideration of additions such as GGBS or fly ash. Whilst the former ultimately provides high strength at a later age it is recognised that incorporating GGBS with CEM I to provide a binary blended concrete causes slower early age strength development which is clearly indicated in Figs 4.8 to 4.10. In spite of this, however, a report by the Institute of Civil Engineers on "Formwork Setting Times for GGBS Concretes" states that *"where only up to 50% GGBS is used, the reduction in early age strength development has not presented problems significant enough to prompt much field investigation."*

Unless the laboratory testing procedure can replicate the conditions of in situ concrete differences will remain. One of the easiest variables to control is the temperature during the curing process and unless this is controlled during curing differences will definitely occur between cube strengths and in situ concrete, yet this in itself is not controllable for in situ concrete which can cure in temperatures exceeding 20^{o}C and indeed, far below during winter months. GGBS concretes are more sensitive to temperatures than CEM I concretes in that an increase in temperature can improve the early age strength gain. An increase in curing temperature to 40^{o}C can increase this strength gain by a factor of 2 of 4 (LERM, 2001) making GGBS concretes suitable for fast track construction, and in many cases heat beds are used to encourage and accelerate early age strength gain (Barnett et al, 1995).

Depending on the structure and its location it is reasonable to require only a medium strength concrete in certain circumstances, instead of a high strength concrete thus making both an economical and environmental sound decision. Naturally where necessary high strength concretes must be used Jaturapitakkul et al (*2004*) refer the high strength of a concrete to exceed 41 N/mm^2 at 28 days. With this in mind a threshold was established as a guideline to the strength value of ternary concretes and concretes exceeding this threshold are considered together with the trade of with ECO_2. Medium strength should not be discounted but by discussing those considered to be of higher strength it highlights the greater versatility for ternary concretes. The ternary mixes for both 0.35 and 0.5 w/c ratios exceeded the 41 N/mm^2 threshold at the 35% replacement level with a markedly lower ECO_2 value than the CEM I as shown in Figure 9.3. At 0.65 this threshold was not reached so these mixes were subsequently ruled out for further comparison and ECO_2 trade off.

At the higher 55% replacement level the ternary mixes at the 0.35 w/c ratio, shown in Figure 9.4, also exceed the 41 N/mm^2 threshold. The ternaries for the 0.5 w/c ratio mix group fell just short of this requirement at 28 days. As seen in Figure 9.5 the fly ash ternaries at the 75% level also exceeded the 41 N/mm^2 threshold at 28 days together with the 20% limestone mix at 0.35 w/c ratio.

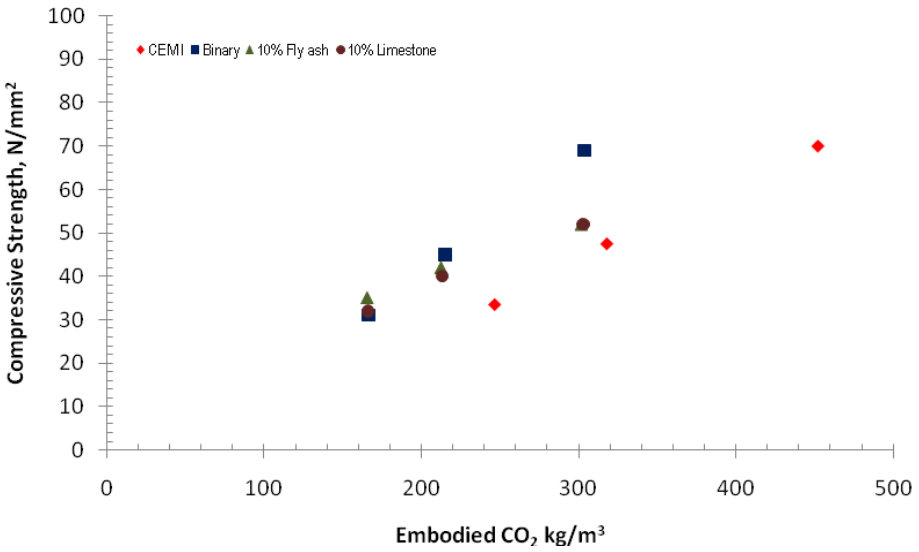


Figure 9.3: Compressive strength against ECO_2 for 35% replacement level mixes at 28 days.

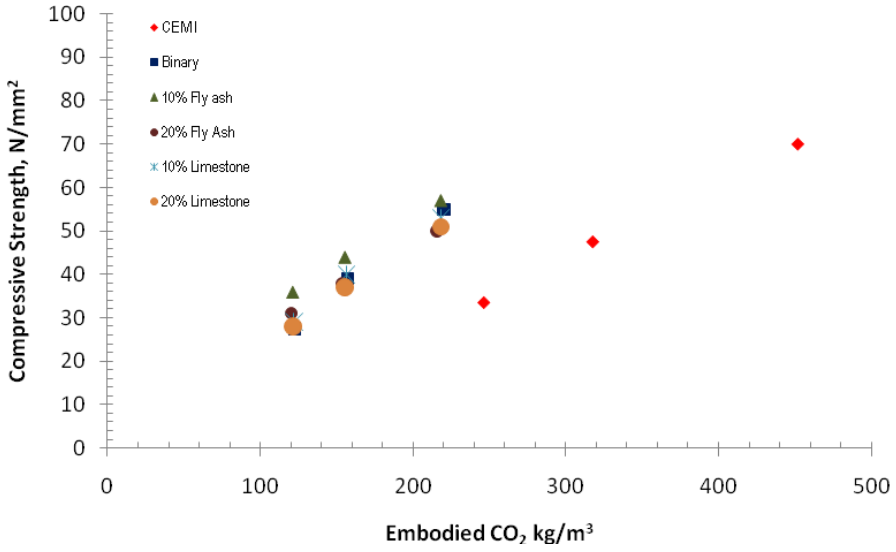


Figure 9.4: Compressive strength against ECO_2 for 55% replacement level mixes at 28 days

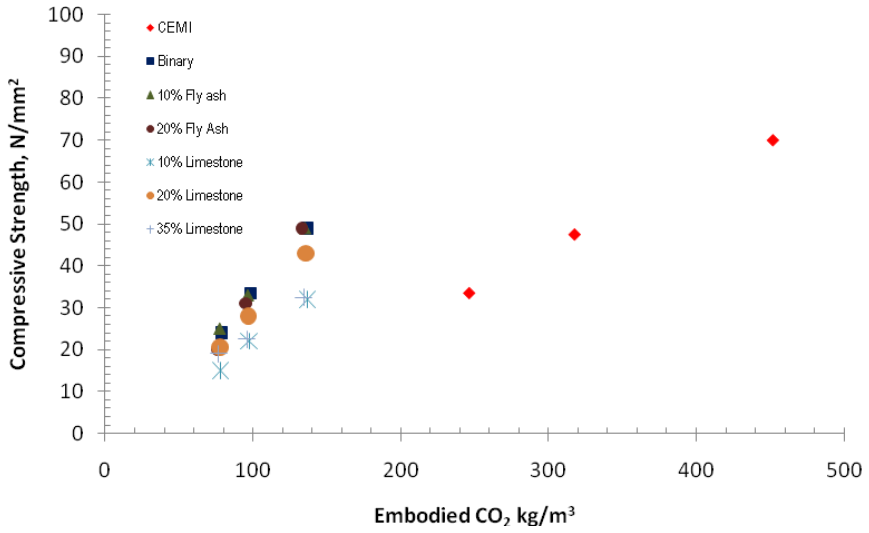


Figure 9.5: Compressive strength against ECO_2 for 75% replacement level mixes at 28 days

To summarise the strength and ECO_2 more effectively Figure 9.6 illustrates the ECO_2 for the mix combinations at the equivalent strength of 40N/mm^2 at 28 days where it is clear that all binary and ternary mixes give a lower ECO_2 than the CEM I. Whilst the strength is paramount to the serviceability of the concrete the other tested properties need to be taken into consideration in order to optimise a durable concrete.

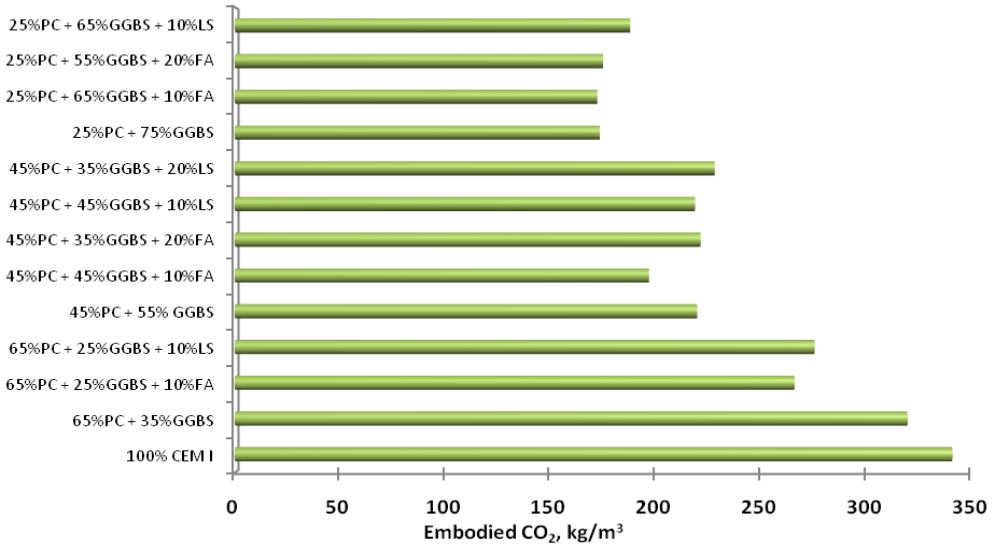


Figure 9.6: ECO_2 for equivalent strength of 40N/mm^2

9.4.2 Absorption and ECO_2 Trade off

For a higher strength concrete both ternaries at the 35% level can be considered at 0.35 and 0.5w/c ratio in addition to all ternary mixes at 55% level for 0.35 w/c ratio. At the higher 75% replacement level both 10% and 20% fly ash ternary mixes together with the 20% limestone ternary may also be considered. However, it cannot be assumed that a high strength concrete is also a durable concrete. The initial surface absorption results for 28 days showed that a concrete with a lower ECO_2, whilst having a high strength may not necessarily prove effective at reducing water absorption by 28 days. Based on BS 1881 an initial absorption of greater than 0.5 ml/m^2 per second (50 x10^{-2} ml/m^2,s) would be considered high whilst less than 0.25 ml/m^2 per second is low. Figure 9.7 indicates that at the 35% level the ternary mixes at all w/c ratios did not show high absorption levels. The 0.35 and 0.5 w/c ratio, all with high strength, also indicated a lower initial surface absorption than the CEM I control mix, this combined with their lower ECO_2, certainly makes them viable concretes thus far, with regard to sustainable and economical benefits.

An increase in GGBS level to 55% increased the initial surface absorption of the ternary concretes. For the higher strength concretes at this level the 0.35 w/c ratio group of ternaries can only be considered and whilst the initial surface absorption had increased they were lower than 0.5 ml/m^2 per second. The 10% limestone ternary was the lowest at 0.36 ml/m^2 per second, this mix is however, higher than the CEM I control mix but it should not be ruled out as a viable mix for certain environments. Figure 9.9 shows the initial surface absorption results for the 75% level against ECO_2 for 28 days. The strength for this mix cannot be considered high at 28 days being only 32 N/mm^2 but may be considered for medium strength concrete should that be sufficient for certain circumstances.

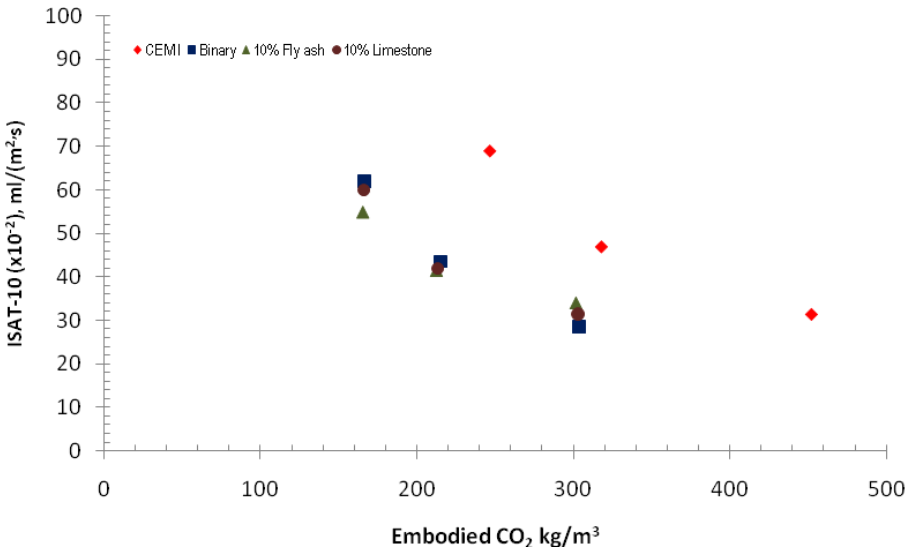


Figure 9.7: ISAT against ECO_2 for 35% replacement level mixes at 28 days.

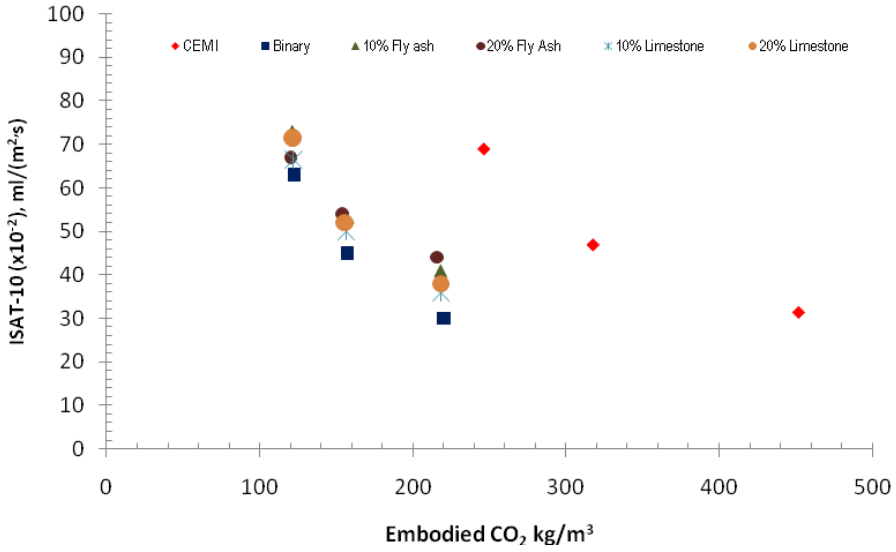


Figure 9.8: ISAT against ECO_2 for 55% replacement level mixes at 28 days.

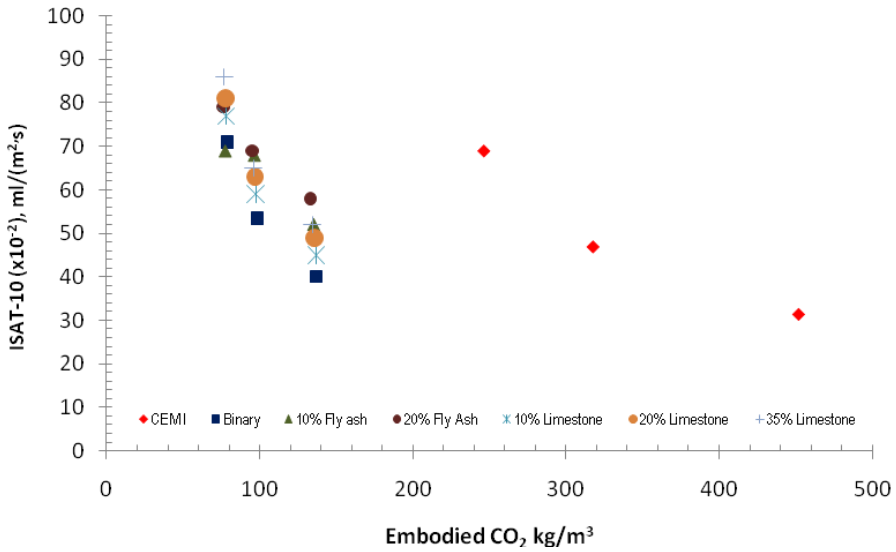


Figure 9.9: ISAT against ECO_2 for 75% replacement level mixes at 28 days.

9.4.3 Air permeability and ECO_2 Trade Off

At the lower 35% level the ternary mixes gave good results against the CEM I with 10% limestone mix providing the better results across the range of w/c ratios as seen in Figure 9.10. The w/c ratio will alter the ECO_2 considerably and it is shown that the lower 0.35 w/c ratio can give much lower ECO_2 values for the binary and ternary mixes than the mid-range, 0.5 w/c ratio. If a higher w/c ratio is required then the 0.5 w/c ratio showed lower air permeability results than the CEM I at 0.65 w/c ratio. At this higher w/c ratio the 10% limestone ternary provides decreased air permeability and ECO_2 than the CEM I control.

An increase to the 55% GGBS level gave a marked increase in intrinsic air permeability as discussed in detail in Chapter 7 and shown in Figure 9.11, therefore possibly ruling these mixes out as viable options for sustainable concrete design although the lower w/c ratio made be considered further. The results followed a similar trend for the water penetration under pressure tests.

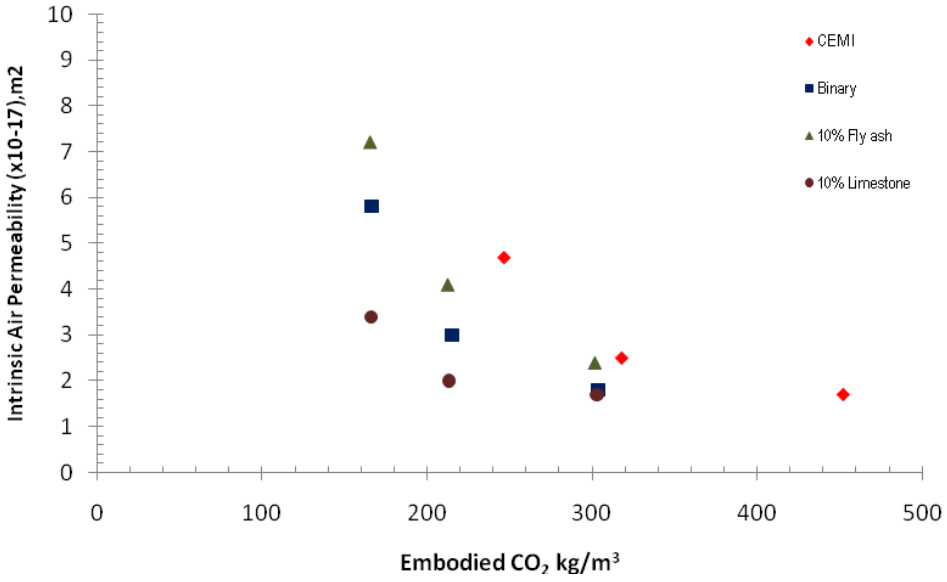


Figure 9.10: Air permeability against ECO_2 for 35% replacement level mixes at 28 days

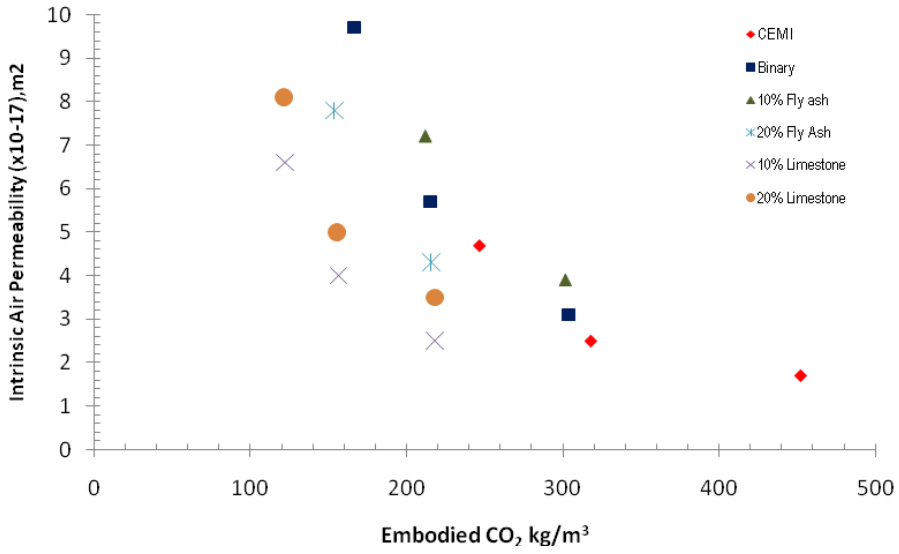


Figure 9.11: Air permeability against ECO_2 for 55% replacement level mixes at 28 days

9.5 Durability and ECO_2 Trade Off

9.5.1 Carbonation

Whilst Chapter 8 highlighted the overall poor resistance to carbonation of the binary and ternary mixes when seen in context with ECO_2 and the CEM I concrete some lower replacement level concretes may still be viable for practical use. The results shown in Figure 9.12, similarly to those shown for air permeability, would suggest the effects of w/c ratio can contribute to lowering the ECO_2. The mix combinations at the lower w/c ratio provide better resistance to carbonation than the CEM I at 0.5 w/c ratio for significantly lower ECO_2. The binary and 10% limestone ternary mix at this 35% replacement level and 0.5 w/c ratio are marginally increased than the CEM I concrete while considerably decreasing the ECO_2 value. At the increased 0.65 w/c ratio these mixes can be considered as viable replacements for CEM I concretes.

An increase in replacement level to 55% shows a clear increase in carbonation, as discussed in detail in Chapter 8, despite their markedly lower ECO_2 as shown in Figure 9.13. The lower 0.35 w/c ratio mix combinations may be considered but will depend on the required mix proportioning and w/c ratio demand for the project. There must be careful consideration when trading resistance to carbonation for ECO_2 and other concrete properties should be taken into consideration as well as the final location placement of the structure.

Chapter 8 discussed the minimum cover recommended by both BS 8500 and BS EN 206. Whilst the latter only refers to CEM I cements BS 8500 considers all cement types. Exposure class XC1 (refer to Table 8.1 for details) recommends a minimum cover of 15mm which will restrict the use of a number of the ternary concretes at the higher w/c ratios but does not exclude those with the lower 0.35 w/c ratio at the 35% addition level that, even by 20 weeks test age show lower depth of carbonation than 10mm, illustrated in Figure 8.1. It was also shown that the 10% ternary concretes and 20% limestone ternary, at the 55% addition level and w/c ratio do not exceed 15mm by 20 weeks. For exposure classes XC2, XC3 and XC4 a greater cover depth is suggested, ranging from 20 to 35mm. At the lower, 0.35 w/c ratio, with considerably lower ECO_2 per kg/m3 compared to CEM I concretes a greater range of addition

level and materials can be considered. Some are also feasible at the 0.5 w/c ratio, again depending on the specific exposure class.

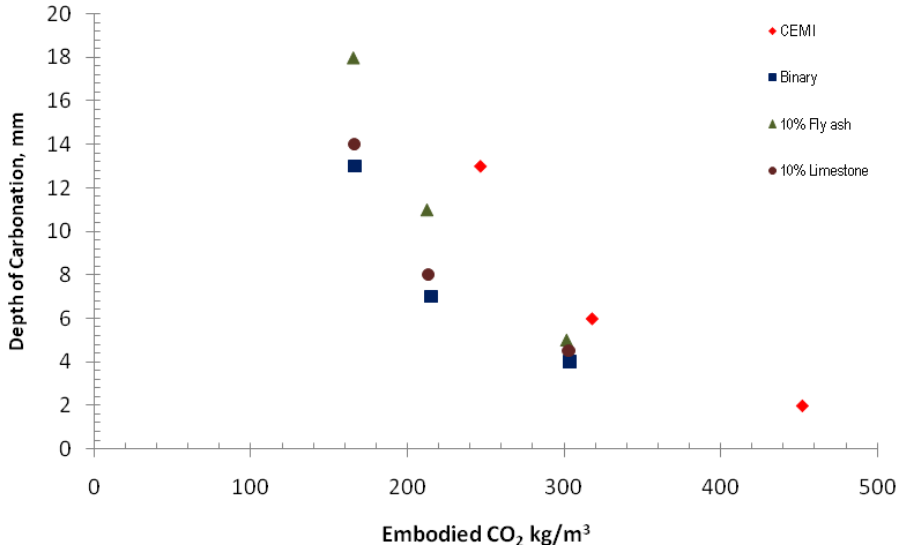


Fig 9.12: Carbonation (8 weeks) against ECO_2 for 35% GGBS level

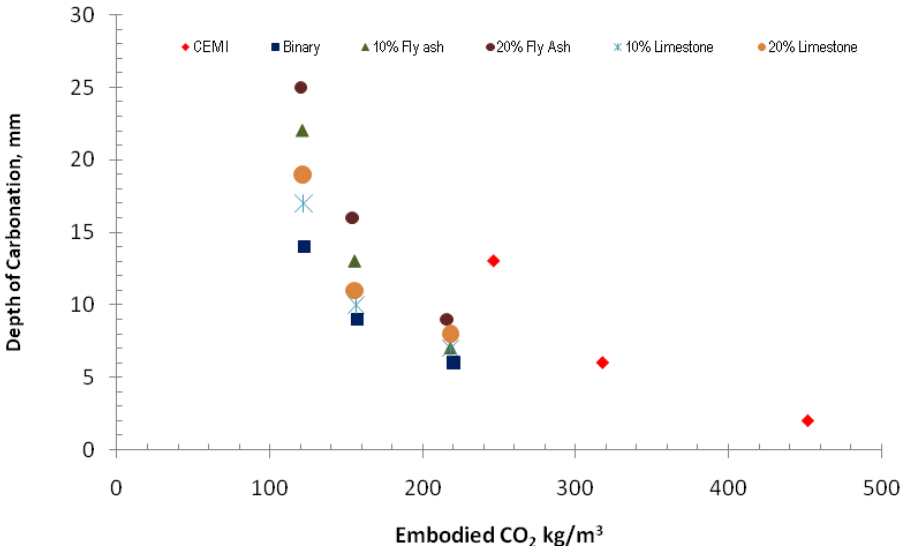


Fig 9.13: Carbonation (8 weeks) against ECO_2 for 55% GGBS level

9.5.2 Chloride Ingress

The previous chapter already discussed the increased resistance to chloride ingress offered by the binary and ternary materials. This combined with the additional properties and the decreased ECO_2 indicates their suitability for use in a practical context. It has been clear that the 10% limestone ternary has the greater potential if all the properties are to be considered and again the chloride ingress result are markedly lower, together with the ECO_2 when compared to CEM I.

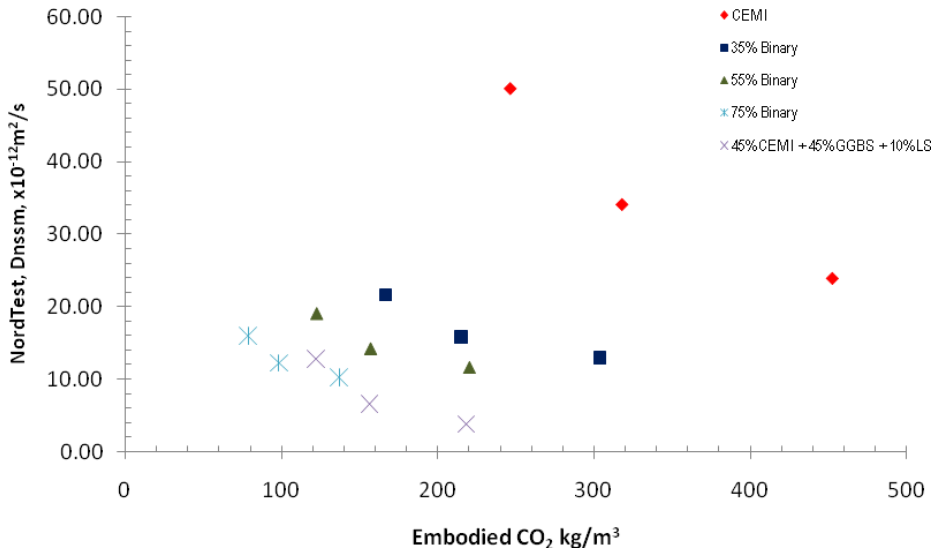


Fig 9.14: Chloride ingress (NordTest) against ECO_2 at 28 days

9.6 Economic Implications for Environmental Concretes

It was alluded to earlier in this chapter that the use of cement replacements such as GGBS and fly ash, are threefold. Improved technical performance has already been discussed at length and remains the main focus of this thesis and the environmental benefits in the reduction of ECO_2 have already been discussed earlier in this chapter. However, given the current state of the construction industry with the present recession it would be prudent to review the basic costs involved in the production of concrete in an “on-site” context.

The material costs used here are based on an average of figures from a number of sources and key suppliers to trade, they are used to simply illustrate possible costs and do not include additional plant costs and actual production costs. As already indicated, to incorporate these figures would require an extensive study into the whole of life costs of each element of cement production and the construction industry as a whole. Table 9.2 outlines the costs used to calculate the material costs per m^3 of concrete shown for each mix combination in Figure 9.15. It is important to note that costs will vary depending on project size which can significantly increase cost savings with volume produced. Market conditions, order quantity, transportation and repeat business will also have some bearing in a practical context. Marked differences were observed when sourcing data for these costing and seemed more apparent with sand and aggregates. The cost per tonne for sand ranged from £13 to £22, and aggregate £18 to £25 per tonne.

Table 9.2: Costings used to calculate total material costs

Material	Cost £ per kg/m^3
CEM I	0.065
GGBS	0.045
Fly Ash	0.02
Limestone	0.076
Sand	0.017
5-10mm Aggregate	0.0215
10-20mm Aggregate	0.021
Water	0.01

It is clear from Figure 9.15 that some modest savings can be made by using replacement materials in mix combinations. Naturally a difference in w/c ratio will also create variance on costs with less material overall required for higher w/c ratios, therefore lowering the costs significantly. Figure 9.16 shows the material costs for the tested mix combinations at an equivalent strength of $40N/mm^2$. Here these costs are put into perspective and indicate that in order to achieve an equivalent strength the varying of the w/c ratio and therefore the volume of material within the mix design may not always have a positive impact on the overall cost to produce the concrete with the 35% binary and 10% limestone ternary at the higher, 75% replacement level, clearly not cost effective. The 10% fly ash at the 55% replacement

shows a significant cost saving but this needs to be taken into consideration with other properties to ensure both a strong and durable concrete.

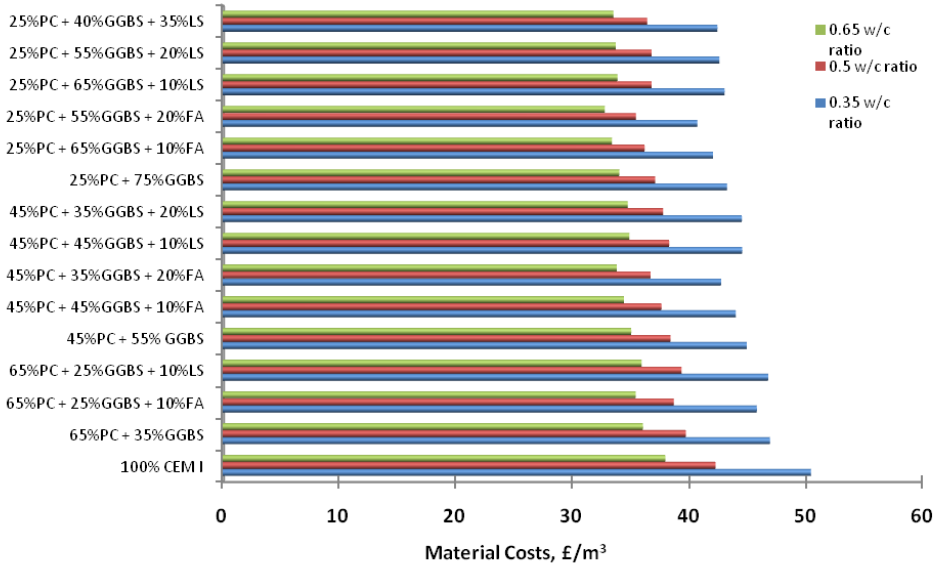


Fig 9.15: Total material costs (£/m³) for each mix combination

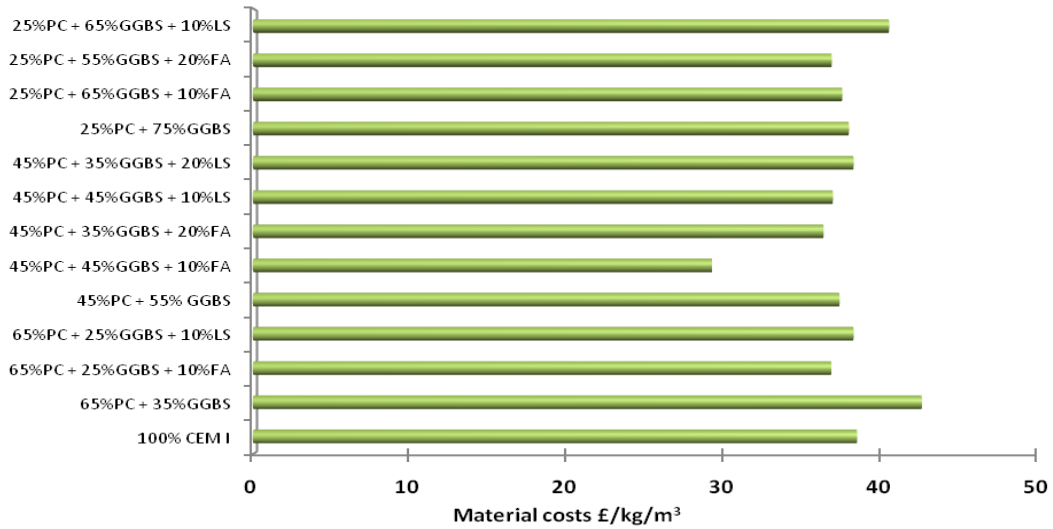


Fig 9.16: Material costs for equivalent strength of 40N/mm²

Table 9.3 provides an overview across the range of tests for selected concretes, figures in green indicate results that are improved on the CEM I control concrete (shown in black together with data that is equal to it), those in red give poorer results by comparison. By reviewing the combined data for selected concretes at equivalent 28 days strength of 40N/mm^2 it can be seen in Table 9.3 that a number of ternary concretes can compete with CEM I in terms of both permeation and durability. Together with their lower ECO_2 and estimated material costs they may indeed warrant further consideration across the cement industry. Across the tested concrete combinations of particular interest are the ternary mixes at the 55% addition level. The 20% fly ash is indicated as outperforming the CEM I concrete across the range of tests shown here, including carbonation when considered at both 28 and 180 day test ages.

Table 9.3: Overall performance of concrete for Equivalent cube strength at 28 days of 40N/mm^2

Mix Combination	ISAT		Sorptivity		Air Permeability		Water Penetration		Carbonation		ECO_2	Material Cost £/kg/m^3
	28 days	180 days	28 days	180 days	28 days	180 days	28 days	180 days	28 days	180 days		
CEM I	57	46	320	255	3.55	3.92	23	16	13	18.5	343	39
65%PC + 35%GGBS	36	24	210	155	4.87	2.64	25.8	12.3	14.5	23	322	43
65%PC + 25%GGBS + 10%PFA	44	32	385	180	7.07	4.99	37.8	14.7	18.5	30	268	37
65%PC + 25%GGBS + 10%LS	42	32	260	185	9.03	5.89	41.6	17	12.5	21	277	38
45%PC + 55% GGBS	45	33	250	185	4.01	2.59	19.4	11	5.5	9	221	38
45%PC + 45%GGBS + 10%PFA	60	37	340	210	2.48	2.1	24.7	12.3	10.5	17	198	29
45%PC + 35%GGBS + 20%PFA	56	32	280	185	3.25	2.26	17.2	10.5	10.5	16.5	223	37
45%PC + 45%GGBS + 10%LS	50	38	260	200	3.12	2.2	18.4	10.4	11.5	19	220	37
45%PC + 35%GGBS + 20%LS	49	33	260	170	5.92	4.69	22.5	10.9	13	18.5	229	38
25%PC + 75%GGBS	48	36	280	200	3.92	3.26	19	8.8	13	21	174	38
25%PC + 65%GGBS + 10%PFA	61	35	245	195	3.32	2.58	17.4	8.2	18	28.5	173	38
25%PC + 55%GGBS + 20%PFA	62	37	230	190	8.37	7.14	28.1	13.4	15	20	176	37
25%PC + 55%GGBS + 20%LS	51	37	245	170	6.48	5.83	42	17.9	15	21	189	41

9.7 Summary

It is evident that there are many practical implications for the use of ternary concretes in modern society. Initially it is important to consider the strength and durability of any concrete when placed in situ as it must always meet with specific requirements with regards to its use and exposure to specific elements that may require it to have good resistance to chloride or carbonation. Overall the ability to reduce the ECO_2 of cement production by over 200kg/tonne in some instances, depending on w/c ratio, cannot be ignored. In this case the ternary blends for the 35% GGBS level at the 0.35 w/c have certainly proved to be worth considering as alternative to the 100% CEM I cement mixes reducing ECO_2 emissions by around 150 kg/tonne, and the 0.5w/c ratio mixes have also shown to be strong and durable. Additional ternary mixes within the 55% level, as already discussed, are also worthy of consideration as they reduce the ECO_2 further by over 200 kg/tonne for the 0.35 w/c ratio.

The basic costs implications were also discussed and it was seen that modest saving could be made by using binary and ternary concrete combinations. Low costs may be more beneficial but market forces can create long term detrimental supply and demand effects. Lower costs can increase use, hence demand, in turn increasing use of the raw materials that are important to the production of concrete. To mitigate it is likely that further environmental taxes are placed on mineral extraction as well as carbon emissions, this again will lead to increases in prices being passed along the supply chain.

The economics in supply and demand are a different and, in themselves an exhaustive issue that do not fall within the remit of this study that is concerned with the practicalities of concrete as in the strength, permeability and durability of ternary based concretes.

CHAPTER TEN:

FINAL CONCLUSIONS & RECOMMENDATIONS FOR FURTHER RESEARCH

10.1 Introduction

The main aim of this study was to develop an understanding of the effects of fly ash and limestone as ternary materials when used together with a CEM I and GGBS base mix, thus enabling the reduction of CO_2 emissions from the production of cement as the main constituent material for concretes. By understanding the effects each addition has on the base mix, it is possible to determine whether it is beneficial to advocate the use of either fly ash or limestone to enhance the strength and durability qualities the binary mixes already processed or what is required to be done to enable their use. In order to gain this knowledge the basic aims were set out in ***Chapter 1***.

The first phase of the study involved characterising the individual materials used. The CEM I and additional materials were found to be consistent with those used in previous studies as discussed in ***Chapter 2***. The GGBS and fly ash were found to be chemically similar to the CEM I but in differing forms and proportions. They both had a higher silica content than the CEM I but a lower CaO. These differing proportions had the effect of reducing early strength development and creating competition between GGBS and fly ash for the free lime from the hydrating cement. The higher silica content of these materials had the effect of increasing C-S-H, forming a denser micro-structure within the cement paste.

Initially the cement combinations ranged from 35% to 90% replacement. However, during the early stage of testing, the 90% level was ruled out, since the setting time was greatly extended and its strength development was similarly impeded. Focus was then centred on 35%, 55% and 75% replacement levels. Overall, it was found that the increasing addition levels

reduced water demand when compared to the CEM I control mix and increased packing density. As expected, SP dosage increased with decreasing in w/c ratio and with increasing in addition level, to give a consistence class of S2, at a fixed water content of 165 l/m^3 in accordance with BS EN 206-1. The inclusion of ternary materials had the effect of reducing the SP dosage. This was more noticeable at the lower w/c ratio of 0.35, where the fines content was higher at the 35% addition level, and across all w/c ratios at the 55% replacement level.

In order to investigate the impact of cement combinations on the cement paste structure the porosity of the cement paste samples was investigated with mercury intrusion porosimetry. It was established that an increase in w/c ratio from 0.35 to 0.5 had the effect of increasing the critical pore diameter in turn causing higher porosity, which decreased with prolonged curing. The data was used to make comparisons with the properties of their concrete counterparts at a later stage. At this point, it was possible to identify certain paste combinations with optimum characteristics in terms of minimum capillary pore size and increased packing density. These included those at the 35% GGBS level across the range of w/c ratios and those at the lower, 0.35 w/c ratio for the 55% GGBS level.

A number of tests were carried out to determine the strength and permeation characteristics of all the cement combinations, as well as their durability properties. These tests, outlined in ***Chapter 3***, were discussed in relation to the estimated ECO2 of all the concretes tested. The overall aim was to determine the benefits and limitations of using combined materials to produce ternary concretes. Whilst conclusions have been summarised, together with discussion concerning likely mechanisms of the effects of additional materials, at the end of each chapter this chapter examines the wider context of the results, highlighting the optimum concrete combinations. It also underlines the practical implications arising. With these conclusions made recommendations for future research will be given.

10.2 Overall Conclusions

Previous studies have clearly indicated that there is strong potential for increasing use of binary concretes within the construction industry. The benefits of GGBS as a binary

constituent have already been discussed but its slower strength gain, whilst an issues for early strength concerns such as the striking of formwork, is most advantageous for the development long-term strength. The purpose of studying the addition of a ternary material to GGBS base mixes was to determine if fly ash or limestone could have a positive effect and increase the earlier strength of the mix as well as improve other aspects such as permeability and durability.

10.2.1 Fresh Properties and Early Age Strength

Overall it was seen from the cement paste mixes that water demand generally decreased with the addition of GGBS for the binary mixes. The fly ash ternary mixes showed a slight increase in water demand when compared to the binary mixes, whilst the packing density was lower. Whilst water demand was comparable to the binary mixes, the packing density was lower. In addition, the paste mixes tested showed an increase in yield stress with the addition of GGBS, this increased further still when limestone and fly ash were incorporated.

The setting times of the pastes increased with w/c ratio and level of GGBS, compared to CEM I. Fly ash, added to the 35% GGBS level at 0.35 w/c ratio, reduced the setting time compared to the binary mix, whilst all other ternary mixes, across the range of w/c ratios showed an increase in setting time compared to that of the CEM I. As expected, a decrease in w/c ratio increased SP dosage requirements. This also increased with the volume of additions, related to the specific surface area of the mixes.

10.2.2 Compressive Strength

With regard to early age strength development of the concretes, it was expected that this would slow down by increasing the level of GGBS. At the lower w/c ratio for the 35% GGBS level, with the inclusion of fly ash and limestone, this effect was exacerbated, but as the level of GGBS increased and with an increase in w/c ratio, the ternary addition provided better results making them more comparable with the binary mixes and, in the case of the 75% GGBS level at the 0.35 w/c ratio, giving improvements compared to this. With this in mind, it was clear that the binary and ternary concretes would take longer to achieve 10 N/mm^2, and this increased with addition level and w/c ratio. Whilst none of the binary or ternary concretes could match CEM I it was seen that the inclusion of limestone generally improved the rate of strength gain

in the early stages for the 35% level, whilst the 10% fly ash ternary concretes showed greater improvement at the 55% level, compared to the limestone. However, there was little difference between these two levels overall.

Despite the indications of early strength gain, more positive effects of GGBS addition were seen after 28 days. Obviously, increasing w/c ratios reduced the compressive strength of concretes, as did the increase in GGBS levels. The 35% GGBS binary mix was comparable with the CEM I by 28 days at all w/c ratios, whilst the other binary concretes were lower. The 55% level did not exceed the strength of the CEM I concrete until 180 and 90 days for the 0.5 and 0.65 w/c ratios respectively. The 75% level gave comparatively poor strength results across the test period.

The addition of ternary materials had differing effects with increasing w/c ratio and GGBS level. At the lower w/c ratio and 35% GGBS level, the effects were negative in that they reduced the long-term strength development compared to the binary mix. The 10% ternary concretes were slightly improved with an increase to the 55% GGBS level. At 0.5 w/c ratio, the 10% ternary mixes were more comparable with the binary concrete for both the 35% and 55% levels, whilst the 20% ternary concretes at the higher level of additions remained lower than the binary. An increase to 0.65 w/c ratio showed the 10% fly ash ternary concrete improved compared to both binary and CEM I concrete by 90 days, whilst the 10% limestone remained comparable with the binary concrete. Again this was noted to a slightly lesser extent at the 55% level.

It was found that it would be possible for all concretes to achieve an equivalent strength of 40 N/mm^2 by 28 days if the w/c ratio was altered for each mix, with lower w/c ratios would be required for the binary and ternary concretes compared to the CEM I.

10.2.3 Absorption & Capillary Rise

Again it was seen that an increase in w/c ratio increased both the ISAT and sorptivity values of the concrete combinations. This was, however, reduced with time. Both the 35% and 55% binary concretes gave reduced absorption values across the range of w/c ratios with the

75% level giving poorer results in contrast to the other addition levels and the CEM I. The 35% level gave better results; the addition of ternary materials gave similar results at the 0.5 and 0.65 w/c ratio. The 10% fly ash ternary concrete at the lower w/c ratio, however, increased the ISAT value. The ternary concretes were again comparable with the binary and CEM I concretes for the 55% level at 0.35 w/c ratios with slight improvements seen at the 0.5 and 0.65 w/c ratios. An increase to the 75% level gave more varied results. The 10% limestone ternary was slightly lower than the CEM I at 0.35 w/c ratio, whilst the other combinations were higher. The higher w/c ratios increased the ISAT values, but at 0.65 w/c ratio both the binary and 10% limestone ternary concretes were lower than CEM I.

The sorptivity results followed the same pattern as the ISAT and both correlated, in general, with the critical pore diameter which increased with rate of absorption.

10.2.4 Permeability

Similar trends occurred to those in the absorption tests, in that permeability increased with w/c ratio and GGBS level. At 28 days, the limestone ternary at the 35% level gave better results across the range of w/c ratios and concretes. Whilst an increase to the 55% level increased the air permeability across the range of concretes, the 10% limestone remained the lowest between binary and ternary concretes, but higher than that of CEM I. An increase to 75% GGBS level significantly increased the air permeability of the binary and ternary concretes. At 180 days, the results followed a similar trend but reduced with the prolonged curing time. The 10% limestone addition for the 35% level showed an improved air permeability for the 0.5 and 0.65 w/c ratio, whilst the fly ash ternary increased the results at this level. For the water penetration tests, the fly ash ternary was more comparable with the CEM I concrete.

The depth of water penetration also increased with critical pore size. In general, the critical pore size increased with the volume of GGBS and again with ternary additions. However, whilst limestone had a higher critical pore size its permeability was lower than that of the fly ash.

10.2.5 Durability

Poor resistance to carbon dioxide ingress for the GGBS binary concretes was expected and increased with w/c ratio and GGBS level. However, the purpose of these tests was to investigate the effects of ternary additions. The binary concretes at 35% and 55% GGBS level were comparable with the CEM I by 20 weeks across the range of w/c ratios but an addition of fly ash increased the depth of carbonation significantly as did limestone addition, although to a lesser extent.

By contrast, the chloride tests gave positive results for the combination concretes in that they were all significantly lower than the CEM I concrete, across the range of w/c ratios for all GGBS levels. The results improved further with increasing levels of GGBS as the concretes capacity to bind chlorides improved. The addition of ternary materials further improved the results at each GGBS level. In some cases the results of the ternary concretes, were one third of the binary results for that GGBS level. For example, the binary at the 35% level (0.5 w/c ratio) measured 13.22 D^{nssm}, m^2/s at 180 days whilst the 10% limestone concrete recorded 4.37 D^{nssm}, m^2/s.

10.2.6 ECO_2 of Concretes Combinations

Across the range of concrete combinations comparisons were made between the ECO_2 per tonne of concrete and the properties of the concretes tested. Essentially the ECO_2 of the binary and ternary concretes were comparable with each other as the proportion of ternary materials was not enough to reduce the ECO_2 significantly compared to the binary concrete given their similar ECO_2 values. However, these mixes gave considerably lower ECO_2 values compared to the CEM I concretes. At 0.35 w/c ratio the ECO_2 for the CEM I concretes was 515 kg/m^3 whilst the binary and ternary concretes gave levels of 380 kg/m^3 reducing further with increasing w/c ratio and cement additions.

The material costs were estimated and it was found that, generally, small savings may be possible for binary and ternary concretes when compared to CEM I concretes. Equivalent 28 day strength of 40 N/mm^2 was estimated across the majority of the tests performed and,

combined with the ECO_2 and material cost data, provided encouraging results with the 20% fly ash at the 55% addition level giving consistently more favourable results than the CEM I.

These results alone do not constitute their use within the concrete industry. They should be viewed in relation to the strength and durability properties of concrete, thus enabling a more informed decision on the use of an optimum concrete that carefully balances sustainability with performance. In light of the test results, it was clear that the use of the 35% range of mixes would be viable across many exposure conditions. They have a comparable strength with the CEM I concretes by 28 days, exceeding them in the longer-term and very good resistance to chloride ingress. Due to their improved permeation and slow rate of penetration of CO_2, it is believed that the ingress of carbon dioxide will be limited to the initial 10mm of the concrete surface. Concretes at the 55% level should not be totally precluded but given consideration for locations where exposure conditions are less aggressive with regards to possible carbonation.

10.3 Recommendations for Future Research

Given the results from this study it was clear that individual properties of each material had a different effect on the microstructure of concrete. It would be beneficial to investigate this further by undertaking a more detailed analysis into the physical and chemical properties of the materials and how they change at a microscopic level. This can incorporate SEM and more detailed porosimetry analysis together with pore fluid chemistry to gain a better understanding of the reactions taking place within the cement paste.

It was found that ternary additions affect the development of strength and durability properties. Whilst these may not have been in an overall positive way an effect was nonetheless seen and further investigation into the use of other materials would be beneficial. Such materials may include silica fume and metakaolin. In addition to ternary blends, there may well be benefit in adding a fourth material to create quaterternary combinations. Other areas may be studied such as the quality and fineness of the materials. The interaction of materials with the aggregates may also be of interest. Varying types of aggregates may be studied including recycled concrete and marginal aggregates.

It was discussed, in ***Chapter*** 8, that the negative effect of using GGBS concretes was the poor resistance to carbonation and how, due to their improved permeation, it was likely that carbonation could be restricted to the initial 10mm of the concrete surface (*Bouikni et al, 2009*). This should be investigated further with a range of exposure conditions, including normal exposure conditions, to investigate this. A wider range of durability tests would be beneficial and should include freeze/thaw effects and external exposure tests including marine environments.

There is a strong argument for the use of ternary concretes by the concrete industry. Indeed, not only do the properties of strength and durability, certainly at the 35% level, allow it, but the ECO_2 values calculated were also positive. However these values are based on basic calculations and the environmental benefits may be far reaching and warrant a greater depth of study. It may be of interest to perform a life cycle analysis (LCA) of these concretes in greater detail in respect of their complete life cycle, including the service-life of a particular structure. This would include a survey of specific elements such as transportation costs and may be studied on a national or global scale. This would involve taking a detailed inventory, as defined by ISO 14040 and 14041, of all the elements of the life-cycle from the production of the concrete to the demolition of the structure at the end of its service life. Allocation procedures in relation to the proportioning of environmental burdens between main products and by-products would also be worthy of further analysis. The impact of raw material extraction, processing and transportation, for example, would be assessed with regards to impacts including those on global warming and energy consumption before making a final evaluation. This would give a greater insight into both the economic and environmental costs and benefits.

These concretes may also have additional beneficial properties that were out with the scope of this study, such as thermal or acoustic, yet may be of interest to industry given the pressure it faces to produce more sustainable and environmentally friendly structures. Concrete may have good thermal inertia but poor acoustic absorption, by studying the effects of additional materials these properties may differ sufficiently to create a balance between the two. Such properties may aid in reducing the running costs during the service life a building,

such as thermal values that may, in turn, reduce insulating or cooling costs, and should be investigated further in order to lend support to the use of these concretes in an ever growing global industry.

REFERENCES & BIBLIOGRAPHY

ABDUL RAZAK, H, CHAI H K, WONG H S, (2004), "Near surface characteristics of concrete containing supplementary cementing materials", *Cement and Concrete Composites* **26**: 883-889

ABDELKADER, B., K. EL-HADJ, et al. (2010). "Efficiency of granulated blast furnace slag replacement of cement according to the equivalent binder concept." *Cement and Concrete Composites* **32**(3): 226-231.

AGARWAL S K, (2006), "Pozzolanic activity of various siliceous materials", *Cement & Concrete Research* **36**: 1735-1739

AHMED M. S., KAYALI O. & ANDERSON W. (2008), Chloride penetration in binary and ternary blended cement concretes as measured by two different rapid methods, Cement and Concrete Composites, Vol. 30, pp. 576–582.

AIQIN W, CHEGZHI Z & NINGSHENG Z, "The theoretic analysis of the influence of the particle size distribution of cement system on the property of cement", *Cement & Concrete Research* **29**: 1721-1726

ALDEA, C. M., SHAH, S. P., KARR, A., "Permeability of cracked concrete", *Materials and Structures* **32**: 370-376

ALEXANDER, M. G. & B. J. MAGEE (1999). "Durability performance of concrete containing condensed silica fume." *Cement and Concrete Research* **29**(6): 917-922.

ALIGIZAKI K. (2006), *Pore structure of cement based materials, testing, interpretation and requirements. Series: Morden Concrete Technology*, V.12, Taylor & Francis, London and New York

ALVES, M. F., R. A. CREMONINI, et al. (2004). "A comparison of mix proportioning methods for high-strength concrete." *Cement and Concrete Composites* **26**(6): 613-621.

AMERICAN ASSOCIATION OF STATE HIGHWAY AND TRANSPORTATION OFFICIALS. Washington, D.C., USA

AASHTO T-277 - 07. Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration.

AMERICAN CONCRETE INSTITUTE (ACI). Detroit, USA

ACI 201.2R - 08. Guide to durable concrete. ACI Manual of Concrete Practice, 2010, Part 1.

ACI Committee 222R - 01. Protection of metals in concrete against corrosion. ACI Manual of Concrete Practice, 2010, Part 1.

ACI Committee 318 - 08. Building code requirements for structural concrete. ACI Manual of Concrete Practice, 2010, Part 3.

ACI Committee 365.1R-00: 2000. Service-life prediction-State-of-the-art report. ACI Manual of Concrete Practice, 2010, Part 5.

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM). Philadelphia, USA

ASTM C1202 - 07: 2007 (Originally approved in 1991). Standard test method for electrical indication of concretes ability to resist chloride ion penetration.

ASTM C1556 - 04: 2004 (Originally approved in 2003). Standard test method for determining the apparent chloride diffusion coefficient of cementitious mixtures by bulkdiffusion.

ASTM C1585 - 04: 2004. Standard test method for measurement of rate of absorption of water by hydraulic-cement concretes.

ASTM Standard C 192: 2002. "Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory", ASTM International, West Conshohocken, PA, DOI: 10.1520/C0192_C0192M-07, www.astm.org

ANDRADE, C. (1993). "Calculation of chloride diffusion coefficients in concrete from ionic migration measurements." *Cement and Concrete Research* **23**(3): 724-742.

ALIGIZAKI, K. K. & P. D. CADY (1999). "Air content and size distribution of air voids in hardened cement pastes using the section-analysis method." *Cement and Concrete Research* **29**(2): 273-280.

ALONSO & WESCHE, (1992), "Characterisation of Fly Ash", *Fly Ash in Concrete, Properties and Performance,* Wesche K (ed), RILEM Report 7, E & E FN Spon, New York

ALSHAMSI AM, ALHOSANI KL, YOUSRI KM. Hydrophobic materials, (1997) "Superplasticiser and microsilica effects on setting of cement paste at various temperatures" *Magazine Concrete Res* **49**(179):11 l-5.

ALSHAMSI AM, SABOUNI AR, BUSHLAIBI AH. (1993) "Influence of set-retarding superplasticisers and microsilica on setting times of pastes at various temperatures" *Cement Concrete Research* **23:**

ANTIOHOS, S. K., V. G. PAPADAKIS, et al. (2007). "Improving the performance of ternary blended cements by mixing different types of fly ashes." *Cement and Concrete Research* **37**(6): 877-885.

ANTIOHOS, S. K., D. PAPAGEORGIOU, et al. (2007). "Mechanical and durability characteristics of gypsum-free blended cements incorporating sulphate-rich reject fly ash." *Cement and Concrete Composites* **29**(7): 550-558.

AUSTIN, S. A., P. J. ROBINS, ET al. (1992). "Influence of curing methods on the strength and permeability of GGBFS concrete in a simulated arid climate." Cement and Concrete Composites 14(3): 157-167.

BABU, K. G., & KUMAR, V. S. (2000). "Efficiency of GGBS in concrete" *Cement and Concrete Research* , **30**, 1031-1036

BÁGEL, L. (1998). "Strength and pore structure of ternary blended cement mortars containing blast furnace slag and silica fume." *Cement and Concrete Research* **28**(7): 1011-1022.

BAI, J., S. WILD, et al. (2003). "Chloride ingress and strength loss in concrete with different PC-PFA-MK binder compositions exposed to synthetic seawater." *Cement and Concrete Research* **33**(3): 353-362.

BAKER, A. P., CORY, H. P., Early Hydration of Limestone-Filled Cements - in "Blended Cements in Construction, Ed. Swamy, R. N.", 1991, pp 1-15

BAKER W. F., Korista D. S. & Novak L. C. (2007), Burj Dubai: Engineering the world's tallest building, The STRUCTURAL Design of Tall and Special Buildings, Vol. 16, pp. 361–375, Published online 2 November 2007 in Wiley Interscience <http://www.interscience.wiley.com> DOI: 10.1002/tal.418.

BAMFORTH, P. B., (1999), "The water permeability of concrete and its relationship with strength." *Magazine of Concrete Research* **43**: 233-241

BAMFORTH, P. B., What PFA Does to Concrete - in "The Use of PFA in Construction, Eds. Dhir, R. K., Jones, M. R.", 1992

BARNETT , S. J., SOUTSOS, M. N., MILLARD, S. G., BUNGEY, J. H., (2006). "Strength development of mortars containing ground granulated blast-furnace slag: Effect of curing temperature and determination of apparent activation energies." *Cement and Concrete Research* **36**(3): 434-440

BASHEER L, BASHEER P AM & LONG AE, (2005) "Influence of coarse aggregate on the permeation, durability and the microstructure characteristics of ordinary Portland cement concrete." *Construction and Building Materials* **19**:682–690

BCA (2008) "Sheet C1 – Embodied CO_2 of concrete" <http://www.sustainableconcrete.org.uk>

BECKNELL, N. K., HALE, W. M., "Ternary concrete mixtures containing ground granulated blast furnace slag and fly ash" in *Cement Combinations for Durable Concrete*, Eds. Dhir, R. K., Harrison, T. A., Newlands, M. D., 2005, pp 133-142

BENTZ, D P., GARBOCZI, E J., ET. AL., (1999), "Effects of Cement Particle Size Distribution on Performance Properties of Portland Cement-Based Materials." *Cement & Concrete Research* **29:** 1663-1671

BENTZ D P, HANSEN KK, MADSEN H D VALLEE F & GRIESEL E J, (2001) "Drying/hydration in cement pastes during curing" *Materials & Structures* **34:** 557-565

BHARATKUMAR, B. H., R. NARAYANAN, et al. (2001). "Mix proportioning of high performance concrete." *Cement and Concrete Composites* **23**(1): 71-80.

BIER, T. A. (1987). "Influence of type of cement and curing on carbonation progress and pore structure of hydrated cement paste." *Materials Research Society Symp. 85, Pittsburgh, Pa.*

BIJEN J. (1996), *Blast furnace slag cement for durable marine structures*, Stichting Beton Prisma, the Netherlands

BILIM, C., C. D. ATIS, et al. (2009). "Predicting the compressive strength of ground granulated blast furnace slag concrete using artificial neural network." *Advances in Engineering Software* **40**(5): 334-340.

BLESZYNSKI R., HOOTON R.D., THOMAS M.D & ROGERS C.A (2002), "Durability of ternary blend concrete with silica fume and blast furnace slag: laboratory and outdoor exposure site studies, *ACI Materials Journal*, **99** (5), 499-508

BOEL, V., DE SCHUTTER, G., (2006), "Porosity of superplasticised cement paste containing limestone filler." *Advances in Cement Research*, **18**: 97-102

BONAVETTI, V., DONZA, H., et. al., (2003), "Limestone filler cement in low w/c concrete: A rational use of energy." *Cement & Concrete Research*, **33**, 2003, pp 865-871

BONAVETTI, V., H. DONZA, et al. (2000). "Influence of initial curing on the properties of concrete containing limestone blended cement." *Cement and Concrete Research* **30**(5): 703-708.

BONAVETTI, V. L., V. F. RAHHAL, et al. (2001). "Studies on the carboaluminate formation in limestone filler-blended cements." *Cement and Concrete Research* **31**(6): 853-859.

BOUIKNI, A., R. N. SWAMY, et al. (2009). "Durability properties of concrete containing 50% and 65% slag." *Construction and Building Materials* **23**(8): 2836-2845.

BOUSOUBAA, N., ZHANG, M. H., et. al., (1998), "Laboratory produced high volume fly ash blended cements: physical properties and compressive strength of mortars." *Cement & Concrete Research* **28**:1555-1569

BOUZOUBAA, N., ZHANG, M. H., et. al., (1999), "Blended fly ash cements - A review" *ACI Materials Journal* **96**: 641-650

BOUZOUBAA, N, BILODEAU, A., et. al., (2004) "Development of ternary blends for high-performance concrete." *ACI Materials Journal* **101:** 19-29

BRANDT, A. (1995). Cement based composites: materials, properties and performance. E and FN SPON

BRANTZ H. L. AND BEAL D. L. (1990), "Development of suitable mixes for Portland cement concrete containing both fly-ash and granulated blast furnace slag. Concrete for the Nineties", *International Conference on the Use of Fly Ash, Slag, Silica Fume and other Siliceous Materials in Concrete*. Concrete Institute of Australia, Australia. 3-5 September 1990. pp 21.

BRITISH RESEARCH ESTABLISHMENT (BRE, 1989), Proceedings of a seminar of the BRE/BCA/Cement Industry Working Party, Building Research Establishment, Garston, November 1989

BRITISH STANDARDS INSTITUTION (BSI). London, UK

BS 12: 1996. Specification for Portland cement.

BS 1881-124: 1988. Testing concrete, Method for analysis of hardened concrete.

BS 1881-125: 1986. Testing concrete, Methods for mixing and sampling fresh concrete in the laboratory.

BS 1881-208: 1996. Testing concrete, Recommendations for the determination of the initial surface absorption of concrete.

BS 5328-1:1997. Concrete - Part 1: Guide to specifying concrete.

BS 6699: 1992. Ground granulated blastfurnace slag for use with Portland cement.

BS 7583: 1996. Specification for Portland limestone cement

BS 7979: 2001. Specification for limestone fines for use with Portland cement.

BS 8110: 1985. (Updated 1997) Structural use of concrete - Part 1. Code of practice for design and construction.

BS 8110: 1985. Structural use of concrete - Part 2. Code of practice for special Circumstances.

BS 8500-1: 2002. Concrete - Complementary British Standard to BS EN 206-1. Method of specifying and guidance for the specifier (No longer current but cited in building regulations).

BS 8500-2: 2002. Concrete - Complementary British Standard to BS EN 206-1. Specification for constituent materials and concrete (No longer current but cited in building regulations).

BS 8500-1: 2006. Concrete - Complementary British Standard to BS EN 206-1. Method of specifying and guidance for the specifier.

BS 8500-2: 2006. Concrete - Complementary British Standard to BS EN 206-1. Specification for constituent materials and concrete.

BS EN 196-1: 2005. Methods of testing cement. Determination of strength

BS EN 196-2: 2005. Methods of testing cement. Chemical analysis of cement

BS EN 196-3: 2005. Methods of testing cement. Determination of setting time and soundness

BS EN 197-1: 2000. Cement - Part 1. Composition, specification and conformity criteria for common cements

BS EN 206-1: 2000. Concrete - Part 1: Specification, performance, production and conformity

BS EN 450-1: 2005. Fly ash for concrete. Definition, specifications and conformity criteria

BS EN 933-1: 1997. Test for geometrical properties of aggregates. Determination of particle shape - Sieving method.

BS EN 933-3: 1997. Test for geometrical properties of aggregates. Determination of particle shape. Flakiness index.

BS EN 933-4: 2001. Test for geometrical properties of aggregates. Determination of particle shape - Shape index.

BS EN 933-6: 2001. Test for geometrical properties of aggregates. Determination of particle shape - Flakiness index.

BS EN 934-1: 2008. Admixtures for concrete, mortar and grout. Common requirements.

BS EN 1008: 2002. Mixing water for concrete - Specification for sampling, testing and assessing the suitability of water, including water recovered from processes in the concrete industry, as mixing water for concrete.

BS EN 1097-3: 1998. Tests for mechanical and physical properties of aggregates. Determination of loose bulk density and voids.

BS EN 1097-6: 2000. Tests for mechanical and physical properties of aggregates. Determination of particle density and water absorption.

BS EN 1990:2002 +A1:2005. Eurocode - Basis of structural design.

BS EN 1992-1-1:2004. Eurocode 2: Design of concrete structures - Part 1-1: General rules and rules for buildings.

BS EN 12350-2: 2009. Testing fresh concrete - Part 2: Slump test.

BS EN 12350-6: 2009. Testing fresh concrete - Part 6: Density test.

BS EN 12390-1: 2000. Testing hardened concrete - Part 1: Shape, dimensions and other requirements for specimens and moulds.

BS EN 12390-2: 2000. Testing hardened concrete - Part 2: Making and curing specimens for strength tests.

BS EN 12390-3: 2002. Testing hardened concrete - Part 3: Compressive strength of test specimens.

BS EN 12620: 2002. Aggregates for concrete.

BS EN 13055-1: 2002. Lightweight aggregates for concrete, mortar and grout.

BS EN 13263-1 and 2: 2005. Silica fume for concrete.

BS EN 15167-1: 2006. Ground granulated blastfurnace slag for use in concrete, mortar and grout - definitions, specifications and conformity criteria.

BS ISO 5725-1: 1994. Accuracy (truness and precision) of measurement methods and results - Part 1. General principles and definitions.

BS ISO 5725-2: 1994. Accuracy (truness and precision) of measurement methods and results - Part 2. Basic method for the determination of repeatability and reproducibility of a standard measurement method.

BS ISO 5725-4: 1994. Accuracy (truness and precision) of measurement methods and results - Part 4. Basic methods for the determination of the truness of a standard measurement method.

CP 110:1972 (revised 1977). Code of practice for the structural use of concrete.

CP 114: 1957. The structural use of reinforced concrete in buildings.

BROOKBANKS P (1989), "Properties of fresh concrete" *Proceedings of BRE/BCA seminar, Performance of limestone filled cements*, Garston 4.1-4.15

BROOKS, J. J., M. A. MEGAT JOHARI, et al. (2000). "Effect of admixtures on the setting times of high-strength concrete." *Cement and Concrete Composites* **22**(4): 293-301.

BUKKI R (1986) "Additives and blended cements from an industrial point of view: A special report" *The International Congress on Cement Chemistry,* Rio de Janerio, Brasil, 1986

CAMPBELL A D & & ROPER H (1996), *Concrete Structures: Materials, Maintenance and Repair,* Longman Scientific & Technical Co, London

CARÉ, S. (2008). "Effect of temperature on porosity and on chloride diffusion in cement pastes." *Construction and Building Materials* **22**(7): 1560-1573.

CARRASCO, M. F., G. MENÉNDEZ, et al. (2005). "Strength optimization of "tailor-made cement" with limestone filler and blast furnace slag." *Cement and Concrete Research* **35**(7): 1324-1331.

CEMBUREAU, (2010) CEMBUREAU, Brussels, accessed 5th July 2011, <http://www.cembureau.be/sites/default/files/worldproduction2010.pdf>

CEMENT HISTORY, accessed 5th May 2011, <http://www.understanding-cement.com/hostory.html>

CHANG, C.-F. & J.-W. CHEN (2006). "The experimental investigation of concrete carbonation depth." *Cement and Concrete Research* **36**(9): 1760-1767.

CHANG, P.-K. (2004). "An approach to optimizing mix design for properties of high-performance concrete." *Cement and Concrete Research* **34**(4): 623-629.

CHEN, C., G. HABERT, et al. (2010). "Environmental impact of cement production: detail of the different processes and cement plant variability evaluation." *Journal of Cleaner Production* **18**(5): 478-485.

CHEN C, HABERTA G, BOUZIDIB Y, JULLIEN A, VENTURAC A (2010). "LCA allocation procedure used as an incitative method for waste recycling: An application to mineral additions in concrete" Resources, Conservation and Recycling **54** (2010) 1231–1240

CHENG, A., R. HUANG, et al. (2005). "Influence of GGBS on durability and corrosion behavior of reinforced concrete." *Materials Chemistry and Physics* **93**(2-3): 404-411.

CHERN, J.-C. & CHAN, Y.-W., (1989) "Deformations of Concrete Made with Blast-Furnace Slag Cement and Ordinary Portland Cement," *ACI Materials Journal*, **86**(4): 872-382.

CHINDAPRASIRT, P., S. HATANAKA, et al. (2008). "Cement paste characteristics and porous concrete properties." *Construction and Building Materials* **22**(5): 894-901.

CHINDAPRASIRT, P., S. HATANAKA, et al. (2009). "Effects of binder strength and aggregate size on the compressive strength and void ratio of porous concrete." *International Journal of Minerals, Metallurgy and Materials* **16**(6): 714-719.

CHINDAPRASIRT, P., C. JATURAPITAKKUL, et al. (2005). "Effect of fly ash fineness on compressive strength and pore size of blended cement paste." *Cement and Concrete Composites* **27**(4): 425-428.

CIRIA (2004) "Formwork Striking Times—criteria, prediction and methods of assessment" CIRIA Report 136

CLAISSE, P A ELSAYAD H I & SHAABAN I G (1999) "Permeability and Pore Volume of Carbonated Concrete" ACI materials Journal. Vol **96** No.3 May 99 pp.378-381

COOK, R. A. & HOVER, K. C., (1999), "Mercury porosimetry of hardened cement pastes." *Cement & Concrete Research* **29**: 933-943

Concrete Experts International, (2006) Carbonation of Concrete http://www.**concrete**-experts.com/pages/carb.htm (Accessed 1/05/2012)

CONCRETE SOCIETY (1991), The use of GGBS and PFA in concrete, Technical Report No. 40, ISBN 0 946691 40.1, The Concrete Society

CUI, L. & J. H. CAHYADI (2001). "Permeability & pore structure of OPC paste." *Cement and Concrete Research* **31**(2): 277-282.

CURRAN M A, (1996). Environmental Life-cycle assessment, McGraw-Hill, London

CYR, M., P. LAWRENCE, ET AL. (2006). "Efficiency of mineral admixtures in mortars: Quantification of the physical and chemical effects of fine admixtures in relation with compressive strength." *Cement and Concrete Research* **36**(2): 264-277.

DAMINELI, B. L., F. M. KEMEID, et al. (2010). "Measuring the eco-efficiency of cement use." *Cement and Concrete Composites* **32**(8): 555-562.

DAMTOFT, J. S., J. LUKASIK, et al. (2008). "Sustainable development and climate change initiatives." *Cement and Concrete Research* **38**(2): 115-127.

DAVIDOVITS J, (2004) *Up to 80% reduction of CO_2 greenhouse gas emission during cement manufacture*, Geoplayer Institute, <http://www.geoplayer.org/library

DAVIDSON, C. I., C. T. HENDRICKSON, et al. (2010). "Preparing future engineers for challenges of the 21st century: Sustainable engineering." *Journal of Cleaner Production* **18**(7): 698-701.

DAY K W (1999), *Concrete mix design, quality control and specification*, 2nd Edition, E & FN spon

DE LARRARD, F., SEDRAN, T., (1994), "Optimization of ultra-high-performence Concrete by the use of a Packing Model" *Cement & Concrete Research* **24:** 997-1009

DEHGHANIAN, CHANGIZ, ARJEMANDI, MOSIEB, (1997) "Influence of Slag Blended Cement Concrete on Chloride Diffusion Rate" *Cement & Concrete Research* **27**: 937-945

DEMIRBOGA, R. (2007). "Thermal conductivity and compressive strength of concrete incorporation with mineral admixtures." *Building and Environment* **42**(7): 2467-2471.

DEQUIEDT, A.-S., M. COSTER, et al. "Distances between air-voids in concrete by automatic methods." *Cement and Concrete Composites* **23**(2-3): 247-254.

DETWEILER R J, BHATTY J I & BHATTACHARJA S (1996). *Supplementary Cementing Materials for Use in Blended Cements*, PCA, USA

DEWAR, J. D., Computer Modelling of Concrete Mixtures, 1999

DE WEERDT, K., M. B. HAHA, et al. (2011). "Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash." *Cement and Concrete Research* **41**(3): 279-291

DHIR R. K., HEWLETT P. C. & CHAN Y. N (1989a), "Near surface characteristics of concrete: intrinsic permeability". *Magazine of Concrete Research*, Vol. **41**, pp. 87–97.

DHIR R. K., HEWLETT P. C. & CHAN Y. N. (1989b), "Near surface characteristics of concrete: prediction of carbonation resistance". *Magazine of Concrete Research*, Vol. **41**, pp. 122–128.

DHIR, R. K., BYARS, E. A.,(1991) " PFA Concrete: Near Surface Absorption Properties" *Magazine of Concrete Research* **43**: 219-232

DHIR, R. K., BYARS, (1993) "PFA concrete: intrinsic permeability" *ACI Materials Journal,* **90:** 571-580

DHIR, R. K., M. A. K. EL-MOHR, et al. (1996). "Chloride binding in GGBS concrete." *Cement and Concrete Research* **26**(12): 1767-1773.

DHIR, R. K., HEWLETT, P. C., et. al., (1994),Estimating the Durability of Concrete in Structures, Concrete,

DHIR, R. K., HEWLETT, P. C., et. al., (1995), "A new technique for measuring the air permeability of near-surface concrete" *Magazine of Concrete Research* **47**: 167-176

DHIR, R. K., P. C. HEWLETT, et al. (1999). "Chemical profiles of cement pastes exposed to a chloride solution spray." *Cement and Concrete Research* **29**(5): 667-672.

DHIR, R. K., SHAABAN, I. G., et. al.,(1993), Preconditioning in situ concrete for permeation testing - Part 1: Initial surface absorption", *Magazine of Concrete Research* **45:** 113-118

DIAMOND, S. (2000). "Mercury porosimetry: An inappropriate method for the measurement of pore size distributions in cement-based materials." *Cement and Concrete Research* **30**(10): 1517-1525

DIAS, W. P. S., (2004) "Influence of drying on concrete sorptivity" *Magazine of Concrete Research* **56**:537-543

DOMONE, P. L. (2006). "Self-compacting concrete: An analysis of 11 years of case studies." *Cement and Concrete Composites* **28**(2): 197-208.

DOUGLAS, E. & G. POUSKOULELI (1991). "Prediction of compressive strength of mortars made with portland cement - blast-furnace slag - fly ash blends." *Cement and Concrete Research* **21**(4): 523-534.

DUCHESNE, J. & M. A. BÉRUBÉ (1994). "The effectiveness of supplementary cementing materials in suppressing expansion due to ASR: Another look at the reaction mechanisms part 2: Pore solution chemistry." *Cement and Concrete Research* **24**(2): 221-230.

ECOBA, 2011, <http://www.ecoba.com/ecobaccpprod.html>

ELAHI, A., P. A. M. BASHEER, et al. (2010). "Mechanical and durability properties of high performance concretes containing supplementary cementitious materials." *Construction and Building Materials* **24**(3): 292-299.

ELKEM MATERIALS LTD (1994), Technical Note, March 1994

ELKEM (2001) http://www.materials.elkem.com/dav/b773e7d942.pdf

EREN 0, BROOKS JJ, CELIK T. (1995) "Setting of fly ash and slag-cement concrete as affected by curing temperature" *Cement, Concrete, and Aggregates* **17**(1):1-7

ERDEM, T. K. & Ö. KIRCA (2008). "Use of binary and ternary blends in high strength concrete." *Construction and Building Materials* **22**(7): 1477-1483.

ESCALANTE-GARCIA, J. I., SHARP, J. H., (2004) "The microstructure and Mechanical properties of blended cements hydrated at temperatures" *Cement & Concrete Research* **31**: 695-702

ESCALANTE-GARCIA, J. I. & J. H. SHARP (2004). "The chemical composition and microstructure of hydration products in blended cements." *Cement and Concrete Composites* **26**(8): 967-976.

EUROPEAN UNION. (2008) Directive 2008/98/EC of the European parliament and of the council on waste and repealing certain directives. Off J Eur Union 2008; L312:3–30.

FABBRI, A., J. CORVISIER, et al. (2009). "Effect of carbonation on the hydro-mechanical properties of Portland cements." *Cement and Concrete Research* **39**(12): 1156-1163.

FELDMAN, R. F. & J. J. BEAUDOIN (1976). "Microstructure and strength of hydrated cement." Cement and Concrete Research 6(3): 389-400.

FERRARIS, C. F., K. H. OBLA, et al. (2001). "The influence of mineral admixtures on the rheology of cement paste and concrete." *Cement and Concrete Research* **31**(2): 245-255.

FLOWER D J M & SANJAYAN J G (2007). "Green house gas emissions due to concrete manufacture." *Int J LCA*, **12** (5): 282-288

FRAAY A.L.A., BIJEN J.M. & DE HAAN Y., (1989) "The reaction of fly ash in concrete: a critical examination", *Cement & Concrete Research,* **19** (2):235-46

FRANCIS A. J., (1977) *The Cement Industry 1796-1914: A History*, David & Charles, London

FULTON F S, (1974), "The properties of Portland cement containing milled ground granulated blast furnace slag", Portland Cement Institute, Johannesburg, South Africa

GALLIAS J L, KARA-ALI R & BIGAS J P, (2000) "The effect of fine material admixtures on water requirements of cement paste" *Cement & Concrete Research*, **30:** 1543-1549

GANESH BABU, K. & G. SIVA NAGESWARA RAO (1996). "Efficiency of fly ash in concrete with age." *Cement and Concrete Research* **26**(3): 465-474.

GANESH BABU, K. & V. SREE RAMA KUMAR (2000). "Efficiency of GGBS in concrete." *Cement and Concrete Research* **30**(7): 1031-1036.

GANJIAN, E. & H. S. POUYA (2009). "The effect of Persian Gulf tidal zone exposure on durability of mixes containing silica fume and blast furnace slag." *Construction and Building Materials* **23**(2): 644-652.

GAO, J. M., C. X. QIAN, et al. (2005). "ITZ microstructure of concrete containing GGBS." *Cement and Concrete Research* **35**(7): 1299-1304.

GARBOCZI E J, (1990), "Permeability, diffusivity and microstructural parameters: A critical review" *Cement and Concrete Research* **20** (4): 503–514.

GARBOCZI, E. J. & D. P. BENTZ (1996). "Modelling of the microstructure and transport properties of concrete." *Construction and Building Materials* **10**(5): 293-300.

GARCI JUENGER, M. C. & H. M. JENNINGS (2001). "The use of nitrogen adsorption to assess the microstructure of cement paste." *Cement and Concrete Research* **31**(6): 883-892.

GARTNER, E. (2004). "Industrially interesting approaches to "low-CO2" cements." *Cement and Concrete Research* **34**(9): 1489-1498.

GESOGLU, M., E. GÜNEYISI, et al. (2009). "Properties of self-compacting concretes made with binary, ternary, and quaternary cementitious blends of fly ash, blast furnace slag, and silica fume." *Construction and Building Materials* **23**(5): 1847-1854.

GHRICI, M., S. KENAI, et al. (2007). "Mechanical properties and durability of mortar and concrete containing natural pozzolana and limestone blended cements." *Cement and Concrete Composites* **29**(7): 542-549.

GIERGICZNY, Z., M. A. GLINICKI, et al. (2009). "Air void system and frost-salt scaling of concrete containing slag-blended cement." *Construction and Building Materials* **23**(6): 2451-2456.

GOGGINS, J., T. KEANE, et al. (2010). "The assessment of embodied energy in typical reinforced concrete building structures in Ireland." *Energy and Buildings* **42**(5): 735-744.

GONEN T & YAZICIOGLU S. (2007), The influence of mineral admixtures on the short and long-term performance of concrete. Building and Environment, Vol. 42, pp. 3080–3085.

GONNERMAN H F & LERCH W (1951) "Changes in characteristics of Portland cement as exhibited in laboratory tests over the period 1904 to 1950" *ASTM Sp Tech Pub No 127*

GOLTERMANN, P., JOHANSEN, V., PALBOL, L., (1997), "Packing of Aggregate: An Alternative Tool to Determine the Optimal Aggregate Mix" *ACI Materials Journal*, **94**: 435-443

GOWRIPALAN, N. & H. M. MOHAMED (1998). "Chloride-ion induced corrosion of galvanized and ordinary steel reinforcement in high-performance concrete." *Cement and Concrete Research* **28**(8): 1119-1131.

GRATTAN-BELLEW, P. E. (1996). "Microstructural investigation of deteriorated Portland cement concretes." *Construction and Building* Materials **10**(1): 3-16.

GUEMMADI, Z., ESCADEILLAS, G., et. al., Influence of limestone fillers on the mechanical performances of cement pastes - in "Cement Combinations for Durable Concrete, Eds. Dhir, R. K., Harrison, T. A., Newlands, M. D.", 2005, pp 339-350

HALE M., RUSSELL B. & BUSH T., (2002) "An assessment of the rapid chloride ion penetrability test", in *Proceedings of the International Conference on concrete for extreme conditions,* Scotland, University of Dundee, p 447-56

HALL C., (1977) "Water movement in porous buildings materials: 1. Unsaturated flow theory and its applications" *Build. Environ.* **12** (1): 117–125.

HALL C., (1989) "Water sorptivity of mortars and concretes: A review", *Magazine of Concrete Research,* **41**(147): 51-61

HABERT G, (2012) "A method for allocation according to the economic behaviour in the EU-ETS for by-products used in cement industry" Int J Life Cycle Assess DOI 10.1007/s11367-012-0464-1

HANEHARA, S., F. TOMOSAWA, et al. (2001). "Effects of water/powder ratio, mixing ratio of fly ash, and curing temperature on pozzolanic reaction of fly ash in cement paste." *Cement and Concrete Research* **31**(1): 31-39.

HANSON (2010), <http://www.heidelbergcement.com/uk/en/hanson>

HANZIC, L., L. KOSEC, et al. (2010). "Capillary absorption in concrete and the Lucas-Washburn equation." *Cement and Concrete Composites* **32**(1): 84-91.

HANZIC, L., ILIC, R., (2003) "Relationship Between Liquid Sorptivity and Capillarity in Concrete" *Cement & Concrete Research*, **33**: 1385-1388

HAQUE, M. N. & T. CHULILUNG (1990). "Strength development of slag and ternary blend concrete." *Cement and Concrete Research* **20**(1): 120-130.

HASSAN, K. E., J. G. CABRERA, et al. (2000). "The effect of mineral admixtures on the properties of high-performance concrete." *Cement and Concrete Composites* **22**(4): 267-271.

HENDRIKS C A, WORRELL D, DEJAGER A, BLOK K & RIEMER P, (2004). "Emission reduction of greenhouse gases from the cement industry." accessed 23rd August 2009, <http://www.ieagreen.org.uk/prghgt42.htm>

HEIKAL, M., EL-DIDAMONY, H., MORSY, M., (2000) "Limestone-filled pozzolanic cement" *Cement & Concrete Research*, **30**: 1827-1834

HEWLETT P.C., (1998) *Lea's Chemistry of cement and Concrete: 4th Edition*, Edmundsbury Press Ltd, London

HILL D., (1984) *A History of Engineering in Classical & Medieval Times,* Routledge, London

HIGGINS, D. D. (2003). "Increased sulfate resistance of ggbs concrete in the presence of carbonate." *Cement and Concrete Composites* **25**(8): 913-919

HIGGINS, D. D. (2007). "GGBS and sustainability", Proceedings of the Institute of Civil Engineers, *Conctrucion Materials*, **160** (3): 99-101

HIGGINS, D. D. (2011) Private communication on 8th August 2011

HINCZAK I. ROPER, H. & SOUTH, W. (1992), "Ternary and quaternary cement systems: some engineering properties. Fourth CANMET/ACI International Conference on the Use of Fly-Ash, Silica Fume, Slag and Natural Pozzolanas in Concrete", Supplementary Papers, Istanbul, Turkey, pp. 33–44.

HINCZAK I. & ROPER H. (1990), "Ternary cements: short and long term properties. Concrete for the Nineties, International Conference on the Use of Fly-Ash, Slag, Silica Fume and other Siliceous Materials in Concrete", *Concrete Institute of Australia*, Australia, 3-5 September 1990, pp 1–17.

HOBBS, D. W. (1999). "Aggregate influence on chloride ion diffusion into concrete." *Cement and Concrete Research* **29**(12): 1995-1998.

HOGAN F J & MEUSEL J W, (1991) "Evaluation for durability and strength development of ground granulated blast furnace slag" *Cement & Concrete Aggregates*, **1**(3): 40-52

HOOTON, R. D., Permeability and Pore Structure of Cement Pastes Containing Fly Ash, Slag and Silica Fume - in ASTM STP 897 "Blended Cements, Ed. Frohnsdorff, G.", 1984, pp 128-143

HOOTON R. D. & TITHERINGTON M. P. (2004), Chloride resistance of high-performance concretes subjected to accelerated curing, Cement and Concrete Research, Vol. 34, pp. 1561–1567

HORNAIN, H., J. MARCHAND, et al. (1995). "Diffusion of chloride ions in limestone filler blended cement pastes and mortars." *Cement and Concrete Research* **25**(8): 1667-1678.

HORIGUCHİ K, (1994). "The rate of carbonation in concrete made with blended cement, in *Durability of Concrete*, ACI SP-145, pp917-31

HSE (2002), Cement, HSE, Caerphilly, accessed 5th May 2011 <http:/www.hse.gov.uk/pubns/cis26.pdf>

HUMPHREYS K, MAHASENAN M (2002),*Toward a sustainable concrete industry. Substudy 8, climate change*, World Business Council for Sustainable Development.

HUNTZINGER, D. N. & T. D. EATMON (2009). "A life-cycle assessment of Portland cement manufacturing: comparing the traditional process with alternative technologies." *Journal of Cleaner Production* **17**(7): 668-675.

HWANG C & LIN C, (1986), "Strength development of blended blast furnace slag cement mortars", **ACI SP-91**: 1323-1340

HWANG C.L., J.J. LIU, L.S. LEE, F.Y. LIN, (1996) "Densified mixture design algorithm and early properties of high performance concrete", *J. Chin.Inst. Civil Hydrol. Eng.* **8** (2): 217 – 229

IGARASHI, S., WATANABE, A., (2005), "Kawamura, M., Evaluation of capillary pore size characteristics in high-strength concrete at early ages" *Cement & Concrete Research*, **35**: 513-519

INGRAM K. D. & DAUGHERTY K. E. (1991), A review of limestone additions to Portland cement and concrete. Cement and Concrete Composites, Vol. 13, pp. 165–170

IRASSAR, E. F. (2009). "Sulfate attack on cementitious materials containing limestone filler -- A review." *Cement and Concrete Research* **39**(3): 241-254.

ISO (2006) Environmental management—life cycle assessment—principles and framework; ISO 14040. International Standardisation Organisation

JATURAPITAKKUL, C., K. KIATTIKOMOL, et al. (2004). "Use of ground coarse fly ash as a replacement of condensed silica fume in producing high-strength concrete." *Cement and Concrete Research* **34**(4): 549-555.

JAU, W. C. & D. S. TSAY (1998). "A study of the basic engineering properties of slag cement concrete and its resistance to seawater corrosion." *Cement and Concrete Research* **28**(10): 1363-1371.

JENNINGS, H. M., THOMAS, J. J., et. al., (2007), "A multi-technique investigation of the nanoporosity of cement paste" *Cement & Concrete Research*, **37:** 329-336

JI, T., T. LIN, et al. (2006). "A concrete mix proportion design algorithm based on artificial neural networks." *Cement and Concrete Research* **36**(7): 1399-1408.

JI, TAO, (2005),"Preliminary study on the water permeability and microstructure of concrete incorporating nano-SiO_2", *Cement & Concrete Research*, **35:** 1943-1947

JOHANSEN, V., ANDERSEN, P. J., Particle Packing and Concrete Properties - in "Materials Science of Concrete, Vol. 2, Ed. Skalny, J. P.", 1990, pp 111-147

JONES, M. R., MAGEE, B. J., (2002), "A Mix Constituent Proportioning Method for Concrete Containing Ternary Combinations of Cements" *Magazine of Concrete Research*, **54**: 125-139

JONES, M. R., DHIR, R. K., MAGEE, B. J., (1997), "Concrete Containing Ternary Blended Binders: Resistance to Chloride Ingress and Carbonation" *Cement & Concrete Research*, **27:** 825-831

JONES, M. R. & A. MCCARTHY (2006). "Heat of hydration in foamed concrete: Effect of mix constituents and plastic density." *Cement and Concrete Research* **36**(6): 1032-1041.

JONES M R, ZHENG L & NEWLANDS M D, (2003), "Estimation of the filler content required to minimise voids ratio in concrete" *Magazine of Concrete Research,* **55** (4): 193-202

JONES M R, ZHENG L & NEWLANDS M D, (2002) "Comparison of particle packing models for proportioning concrete constituents for minimum voids ratio" *Materials & Structures*, **35**(6):301-309

JONS, E. S. & B. OSBAECK (1982). "The effect of cement composition on strength described by a strength-porosity model." *Cement and Concrete Research* **12**(2): 167-178.

JOSA, A., A. AGUADO, et al. (2007). "Comparative analysis of the life cycle impact assessment of available cement inventories in the EU." *Cement and Concrete Research* **37**(5): 781-788.

JUENGER, M. C. G., F. WINNEFELD, et al. (2011) "Advances in alternative cementitious binders." Cement and Concrete Research In Press, Corrected Proof.

JUN-YUAN ET AL.(1984), "Hydration of Fly Ash-Portland Cements", Cement & Concrete research, **14**, pp. 505-512

KADRI E H & DUVAL R, (2002). "Effect of ultrafine particles on heart of hydration of cement mortars." *ACI Materials Journal* **99** (2): 138-142

KAUFMANN, J., F. WINNEFELD, et al. (2004). "Effect of the addition of ultrafine cement and short fiber reinforcement on shrinkage, rheological and mechanical properties of Portland cement pastes." *Cement and Concrete Composites* **26**(5): 541-549.

KHEDR SA, ABOU-ZEID MN. U, (1994) "Characteristics of silica-fume concrete" *J Mater Civil Eng* **6**(3):357-75.

KHAN, M. I., C. J. LYNSDALE, et al. (2000). "Porosity and strength of PFA/SF/OPC ternary blended paste." *Cement and Concrete Research* **30**(8): 1225-1229

KHAN, M. I. & C. J. LYNSDALE (2002). "Strength, permeability, and carbonation of high-performance concrete." *Cement and Concrete Research* **32**(1): 123-131.

KHATIB, J. M. & J. J. HIBBERT (2005). "Selected engineering properties of concrete incorporating slag and metakaolin." *Construction and Building Materials* **19**(6): 460-472.

KHAYAT, K. H., AITCIN, P. C., Silica Fume - A Unique Supplementary Cementitious Material - in "Mineral Admixtures in Cement and Concrete, Ed. Ghosh, S. N.", 1993, pp 227-265

Kokobu M & Nagataki S (1989(Carbonation of concrete with fly ash and corrosion of reinforcements in 20 years Tests", *Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete,* **ACI SP-114**: 315-329

KONSTA-GDOUTOS, M. S. & S. P. SHAH (2003). "Hydration and properties of novel blended cements based on cement kiln dust and blast furnace slag." *Cement and Concrete Research* **33**(8): 1269-1276.

KORPA, A. & R. TRETTIN (2006). "The influence of different drying methods on cement paste microstructures as reflected by gas adsorption: Comparison between freeze-drying (F-drying), D-drying, P-drying and oven-drying methods." *Cement and Concrete Research* **36**(4): 634-649.

KOUROUNIS, S., S. Tsivilis, et al. (2007). "Properties and hydration of blended cements with steelmaking slag." *Cement and Concrete Research* **37**(6): 815-822.

KOVLER, K. & N. ROUSSEL (2011), "Properties of fresh and hardened concrete." Cement and Concrete Research In Press, Corrected Proof.

KUMAR R & BHATTACHARJEE ,(2002) " Correlation between initial surface absorption rate of water and in-situ strength of concrete" *Indian Concrete Journal* **76** (4): 231–235

KUMAR, R. & B. BHATTACHARJEE (2003). "Porosity, pore size distribution and in situ strength of concrete." *Cement and Concrete Research* **33**(1): 155-164.

KUMAR, R. & B. BHATTACHARJEE (2003). "Study on some factors affecting the results in the use of MIP method in concrete research." *Cement and Concrete Research* **33**(3): 417-424.

KUMAR, R. & B. BHATTACHARJEE (2004). "Assessment of permeation quality of concrete through mercury intrusion porosimetry." *Cement and Concrete Research* **34**(2): 321-328.

KWAN A K H & MORA C F, (2001). "Effects of various shape parameters on packing of aggregate particles." *Magazine of Concrete Research*, **53** (2): 91-100

LACHEMI, M., K. M. A. HOSSAIN, et al. (2004). "Performance of new viscosity modifying admixtures in enhancing the rheological properties of cement paste." *Cement and Concrete Research* **34**(2): 185-193.

Laldji S & Tagnit-Hamou A, (2006), "Properties of Ternary and Quaternary Concrete Incorporating New Alternative Cementitious Material", *ACI Materials Journal*, **103** (2): 83-89

LANE D. S. & OZYILDIRIM C. (1999), Preventive measures for alkali-silica reactions (binary and ternary systems), Cement and Concrete Research, Vol. 29, pp. 1281–1288.

LANGE, F., H. MÖRTEL, et al. (1997). "Dense packing of cement pastes and resulting consequences on mortar properties." *Cement and Concrete Research* **27**(10): 1481-1488.

LEE, K.-M. & P.-J. PARK (2005). "Estimation of the environmental credit for the recycling of granulated blast furnace slag based on LCA." *Resources, Conservation and Recycling* **44**(2): 139-151.

LEE, T.-C., W.-J. WANG, ET AL. (2009). "Enhancement in early strengths of slag-cement mortars by adjusting basicity of the slag prepared from fly-ash of MSWI." *Cement and Concrete Research* **39**(8): 651-658.

LI, D., SHEN, J., et. al., (2000) "Study of properties on fly ash-slag complex cement" *Cement & Concrete Research*, **30**: 1381-1387

LI, G. & X. ZHAO (2003). "Properties of concrete incorporating fly ash and ground granulated blast-furnace slag." *Cement and Concrete Composites* **25**(3): 293-299.

LIM, C.-H., Y.-S. YOON, et al. (2004). "Genetic algorithm in mix proportioning of high-performance concrete." *Cement and Concrete Research* **34**(3): 409-420.

LIVESEY, P. (1991). "Strength characteristics of Portland-limestone cements." *Construction and Building Materials* **5**(3): 147-150.

LOCKINGTON, D., LEECH, G., et. al., The sorptivity test and predicting resistance to water absorption in concrete - in "Innovations and Developments in Concrete Materials and Construction, Eds. Dhir, R. K. et. al.", 2002, pp 315-324

LONG G C, WANG X Y & XIE XJ (2002) "the influences of mineral admixtures on the packing of properties of fresh pastes", *Journal of Building Materials,* **25**(7): 1501-1511

LONG, G. CH., XIE, Y. J., JIANG, Z. W., (2005) "Efficiency of fly ash in cementitious materials" *Advances in Cement Research,* **17:** 113-119

LONG G, WANG X Y, XIAO R & XIE Y, (2005) "The influences of ultra-fine powders on the compatibility of cement & superplasticiser with very low water/binder ratio", *Advances in Cement Research*,**17**: 113-119

LOOTENS, D., P. JOUSSET, ET al. (2009). "Yield stress during setting of cement pastes from penetration tests." *Cement and Concrete Research* **39**(5): 401-408.

LUO, R., Y. CAI, et al. (2003). "Study of chloride binding and diffusion in GGBS concrete." *Cement and Concrete Research* **33**(1): 1-7.

MAGAROTTO, R., MORATTI, F., ZEMINIAN, N., Characterisation of limestone and fly ash for a rational use in concrete - in "Cement Combinations for Durable Concrete, Eds. Dhir, R. K., Harrison, T. A., Newlands, M. D.", 2005, pp 71-80

MATSCHEI, T., B. LOTHENBACH, et al. (2007). "The role of calcium carbonate in cement hydration." *Cement and Concrete Research* **37**(4): 551-558.

MASSAZZA F, (1987) "The role of additions to cement in the concrete durability", *Cementos*, **84**, (4), 359

McCarthy, M. J., Dhir, R. K., Towards maximising the use of fly ash as a binder, Fuel, 78, 1999, pp 121-132

McCarthy, M. J., P. A. J. Tittle, et al. (2001). "Mix proportioning and engineering properties of conditioned PFA concrete." *Cement and Concrete Research* **31**(2): 321-326.

McLeod R.S., (2005). "Ordinary Portland Cement: with extraordinary high Co_2 emission" accessed 23rd September 2005, <http://www.newbuilder.co.uk/bffmag>

McPolin, D., P. A. M. Basheer, et al. (2005). "Obtaining progressive chloride profiles in cementitious materials." *Construction and Building Materials* **19**(9): 666-673.

Mechling, J.-M., A. Lecomte, et al. (2009). "Relation between cement composition and compressive strength of pure pastes." *Cement and Concrete Composites* **31**(4): 255-262.

Megat Johari, M. A., J. J. Brooks, et al. (2011). "Influence of supplementary cementitious materials on engineering properties of high strength concrete." *Construction and Building Materials* **25**(5): 2639-2648.

Megat Johari, M. A., J. J. Brooks, et al. (2011). "Influence of supplementary cementitious materials on engineering properties of high strength concrete." *Construction and Building Materials* **25**(5): 2639-2648.

Mehta, P K. (1983), Pozzolanic and cementitious by-products as mineral admixtures for concrete - a critical review. In: Malhotra, V M (Ed). Fly ash, silica fume, slag and other mineral by-products in concrete. ACI SP-79, Detroit.

Mehta, P K. (1986), "Effect of fly ash composition on sulfate resistance of concrete" *Journal of the American Concrete Institute,* (6): 994-1000

Mehta, P. K., Monteiro, Paulo J. M.,2006, Concrete: Microstructure, Properties and Materials, McGraw-Hill, London

Mejia, R., Delvasto, S., et. al., (2003) "Chloride Diffusion Measured by a Modified Permeability Test in Normal and Blended Cements" *Advances in Cement Research*, **15**, 2003, pp 113-118

Menadi, B., S. Kenai, et al. (2009). "Strength and durability of concrete incorporating crushed limestone sand." *Construction and Building Materials* **23**(2): 625-633.

Menendez, G., Bonavetti, V., Irassar, E., (2003) "Strength development of ternary blended cement with limestone filler and blast-furnace slag" *Cement and Concrete Composites*, **25**: 61-67

MEUSEL J W & ROSE J H, (1983), " Production of granulated blastfurnace slag at Sparrows Point, and workability and strength potential of concrete incorporating the slag" *Fly Ash, Silica Fume & Other Mineral By-products in Concrete,* **ACI SP-79**: 867-890

MILLER, E. W. (1993). "Blended cements--Applications and implications." *Cement and Concrete Composites* **15**(4): 237-245.

MINDESS S., YOUNG F. J. & DARWIN D. (2003), CONCRETE, 2ND ED., PRENTICE-HALL

MIURA T & IWAKI I, (2000) "Strength development of concrete incorporating high levels of ground granulated blast furnace slag at low temperatures", *ACI Material Journal*, **97** (1), 66-70

MOHR, P., HANSEN, W., et. al., (2000) "Transport properties of concrete pavements with excellent long-term in-service performance" *Cement & Concrete Research*, **30**: 1903-1910

MOHD. ZAIN, M. F., M. NAZRUL ISLAM, et al. (2005). "An expert system for mix design of high performance concrete." *Advances in Engineering Software* **36**(5): 325-337.

MOON, H. Y., H. S. KIM, et al. (2006). "Relationship between average pore diameter and chloride diffusivity in various concretes." *Construction and Building Materials* **20**(9): 725-732.

MORANVILLE-REGOURD, M. (2003). Cements Made from Blastfurnace Slag. Lea's Chemistry of Cement and Concrete (Fourth Edition). Oxford, Butterworth-Heinemann: 637-678.

MOURET, M., E. RINGOT, et al. "Image analysis: a tool for the characterisation of hydration of cement in concrete - metrological aspects of magnification on measurement." *Cement and Concrete Composites* **23**(2-3): 201-206.

MUN, K. J., S. Y. SO, et al. (2007). "The effect of slaked lime, anhydrous gypsum and limestone powder on properties of blast furnace slag cement mortar and concrete." *Construction and Building Materials* **21**(7): 1576-1582.

MUNDAY J G L, ONG L T & DHIR R K, (1983) "Mix proportioning of concrete with PFA, a critical review", in V M Malhotra (Ed) *Proceeding, 1st International Conference on the Use of Fly Ash, Silica Fume and Other Mineral by-products in Concrete*, SP-79, ACI, Detroit pp 267-288

NEHDI, M., MINDESS, S., AITCIN, P. C., (1996), "Optimization of High-strength Limestone Filler Cement Mortars" *Cement & Concrete Research*, **26**: 883-893

NEHDI, M. & S. AL MARTINI (2009). "Estimating time and temperature dependent yield stress of cement paste using oscillatory rheology and genetic algorithms." *Cement and Concrete Research* **39**(11): 1007-1016.

NEHDI, M. & M. A. RAHMAN (2004). "Estimating rheological properties of cement pastes using various rheological models for different test geometry, gap and surface friction." *Cement and Concrete Research* **34**(11): 1993-2007.

NEHDI, M., M. PARDHAN, et al. (2004). "Durability of self-consolidating concrete incorporating high-volume replacement composite cements." *Cement and Concrete Research* **34**(11): 2103-2112.

NEHDI M L & SUMMER J, (2002) "Optimization of ternary cementitious mortar blends using factorial experimental plans" *Materials & Structures* **35**(9): 495-503

Nepper-Christensseen P¸(1979), "Cement" , Aalborg, Denmark

NEVILLE A, (1995) *Properties of Concrete: 4th Edition*, London, Longman

NILSSON, L. O., (2002), "Long term moisture transport in high performance concrete" *Materials and Structures*, **35**: 641-649

NIU Q, FENG N, YANG J & ZHENG X, (2002) "Effect of superfine slag powder on cement properties" *Cement Concrete Research*¸**:** 615-621

NORDTEST, (1999), NT Build 492 " Concrete, Mortar and Cement-Based Repair Materials: Chloride migration coefficient from no-steady state migration" , NORDTEST, Finland

NUMATA S, KOIDE Y & SHIMOKOYASHI S, (1986) "Properties of ultra-highly pulverised granulated blast furnace slag – PC blends" *ACI Special Publication*, **SP-91-66:** 1341-1360

O'BRIEN K, MENACHE J & O'MOORE L (2009). "Impact of fly ash content and fly ash transportation distance on embodied greenhouse gas emissions and water consumption in concrete." *Int J LCA*, May 2009

OGAWA, K., H. UCHIKAWA, et al. (1980). "The mechanism of the hydration in the system C3S-pozzolana." *Cement and Concrete Research* **10**(5): 683-696.

OMAR SAEED BAGHABRA, A.-A. & M. MASLEHUDDIN (1993). "The effect of chloride and sulfate ions on reinforcement corrosion." *Cement and Concrete Research* **23**(1): 139-146.

ONER, A. & S. AKYUZ (2007). "An experimental study on optimum usage of GGBS for the compressive strength of concrete." *Cement and Concrete Composites* **29**(6): 505-514.

O'ROURKE, B., C. MCNALLY, et al. (2009). "Development of calcium sulfate-ggbs-Portland cement binders." *Construction and Building Materials* **23**(1): 340-346.

ORTIZ O, CASTELLS F, SONNEMANN G (2008) Sustainability in the construction industry: a review of recent developments based on LCA. Constr Build Mater **23**:28–39

OSBOURNE G.J., (1986) "Carbonation of blastfurnace slag cement concretes, *Durability of Building Materials,* **4:** 81-96

Ozyildirim C & Halstead W J (1994), Improved concrete quality with combinations of fly ash and silica fume, *ACI Materials Journal*, Vol. **91**(6): 587–594.

PADE, C. & M. GUIMARAES (2007). "The CO2 uptake of concrete in a 100 year perspective." *Cement and Concrete Research* **37**(9): 1348-1356.

PAGE, C. L., N. R. SHORT, et al. (1981). "Diffusion of chloride ions in hardened cement pastes." *Cement and Concrete Research* **11**(3): 395-406.

PANDEY, S. P., A. K. SINGH, et al. (2003). "Studies on high-performance blended/multiblended cements and their durability characteristics." *Cement and Concrete Research* **33**(9): 1433-1436.

PAPADAKIS V.G., VAYENAS C.G. & FARDIS M.N., (1991) "Physical & chemical characteristics effecting the durability of concrete", *ACI Materials Journal,* **88** (2): 186-96

PAPADAKIS, V. G. (1999). "Effect of fly ash on Portland cement systems: Part I. Low-calcium fly ash." *Cement and Concrete Research* **29**(11): 1727-1736.

PAPADAKIS, V. G. (2000). "Effect of supplementary cementing materials on concrete resistance against carbonation and chloride ingress." *Cement and Concrete Research* **30**(2): 291-299.

PAPADAKIS, V. G., S. ANTIOHOS, et al. (2002). "Supplementary cementing materials in concrete: Part II: A fundamental estimation of the efficiency factor." *Cement and Concrete Research* **32**(10): 1533-1538.

PAPADAKIS, V. G. & S. TSIMAS (2002). "Supplementary cementing materials in concrete: Part I: efficiency and design." *Cement and Concrete Research* **32**(10): 1525-1532.

PAPAYIANNI, I., G. TSOHOS, et al. (2005). "Influence of superplasticizer type and mix design parameters on the performance of them in concrete mixtures." *Cement and Concrete Composites* **27**(2): 217-222.

PARK, S. B., D. S. SEO, et al. (2005). "Studies on the sound absorption characteristics of porous concrete based on the content of recycled aggregate and target void ratio." *Cement and Concrete Research* **35**(9): 1846-1854.

PARROTT, L. J., (1994), "Moisture Conditioning and Transport Properties of Concrete Test Specimens" *Materials and Structures*, **27:** 460-468

PARROTT, L. J.,(1995) "Influence of cement type and curing on the drying and air permeability of cover concrete" *Magazine of Concrete Research*, **47:** 103-111

PARROTT, L. J., (1992) "Variations of water absorption rate and porosity with depth from an exposed concrete surface: Effects of exposure conditions and cement type" *Cement & Concrete Research*, **22**: 1077-1088

PÉRA, J., S. HUSSON, et al. (1999). "Influence of finely ground limestone on cement hydration." Cement and *Concrete Composites* **21**(2): 99-105.

PIPILIKAKI, P. & M. KATSIOTI (2009). "Study of the hydration process of quaternary blended cements and durability of the produced mortars and concretes." *Construction and Building Materials* **23**(6): 2246-2250.

PIPILIKAKI, P., M. KATSIOTI, et al. (2009). "Performance of limestone cement mortars in a high sulfates environment." *Construction and Building Materials* **23**(2): 1042-1049.

PIPILIKAKI, P. & M. BEAZI-KATSIOTI (2009). "The assessment of porosity and pore size distribution of limestone Portland cement pastes." *Construction and Building Materials* **23**(5): 1966-1970.

PISTILLI MF, WINTERSTEEN R, CECHNER R. (1984) "The uniformity and influence of silica fume from a U.S. source on the properties of Portland cement concrete", *Cement, Concrete Aggregates* **6**(2): 1204.

PLEAU, R., M. PIGEON, et al. "Some findings on the usefulness of image analysis for determining the characteristics of the air-void system on hardened concrete." *Cement and Concrete Composites* **23**(2-3): 237-246.

POON, C. S., Z. H. SHUI, et al. (2004). "Effect of microstructure of ITZ on compressive strength of concrete prepared with recycled aggregates." *Construction and Building Materials* **18**(6): 461-468.

POON, C. S., Z. H. SHUI, et al. (2004). "Influence of moisture states of natural and recycled aggregates on the slump and compressive strength of concrete." *Cement and Concrete Research* **34**(1): 31-36.

POPPE, A., SCHUTTER, G., (2005), "Cement hydration in the presence of high filler contents" *Cement & Concrete Research*, **35**: 2290-2299

POPOVICS S, (1981) "New formulas for the prediction of the effects of porosity on concrete strength" *ACI Materials Journal,* **78** (2): 127-129

POPOVICS S, (1985) "Generalisations of Abram's Law" *ACI Materials Journal,* **82** (2): 136-146

POWERS T. C., (1958). "Structure & Physical properties of hardened Portland cement paste" *J American Ceramic Society*, **41**:1-6

POWERS TC, COPELAND LE, MANN HM. (1959) "Capillary continuity or discontinuity in cement pastes" *J Portland Cement Assoc Res Dev Lab* **1(**2):38-48.

QIAN, J., C. SHI, et al. (2001). "Activation of blended cements containing fly ash." *Cement and Concrete Research* **31**(8): 1121-1127.

QUILLIN, K., G. OSBORNE, et al. (2001). "Effects of w/c ratio and curing conditions on strength development in BRECEM concretes." *Cement and Concrete Research* **31**(4): 627-632.

RAHHAL, V. & R. TALERO (2005). "Early hydration of Portland cement with crystalline mineral additions." *Cement and Concrete Research* **35**(7): 1285-1291.

RAMACHANDRAN, V. S. & J. J. BEAUDOIN (2001). Handbook of Analytical Techniques in Concrete Science and Technology,. Norwich, NY, William Andrew Publishing

RAMACHANDRAN VS, & MALHOTRA VM. Superplasticisers,1995, In: Ramachandran VS, editor. Concrete Admixtures Handbook, Noyes Publications

RAMACHANDRAN VS & ZHANG C, (1986), "Cement with calcium carbonate additions" *Proceedings of the 8th International Congress on the Chemistry of Cement,* Rio de Janeiro, **11**: 178-187

RAMEZANIANPOUR, A.A., KHADEMI, M. AND ASHRAFI, H.R(2005). "Diffusion coefficient of chloride ions undersimulated conditions. In Cement combinations for durable concrete, Proceedings of the Internationalconference held at UOD, 5-7 July, (2005), Ed. By, Dhir, R.K., Harrison, T.A. and Newlands, M.D.

RAMEZANIANPOUR, A. A., E. GHIASVAND, et al. (2009). "Influence of various amounts of limestone powder on performance of Portland limestone cement concretes." *Cement and Concrete Composites* **31**(10): 715-720.

RILEM, CPC-11.2, (1994). "Absorption of water by concrete by capillarity" TC14-CPC, 1982, RILEM technical recommendations for the testing and use of construction materials, International Union of Testing and Research Laboratories for Materials and Structures, E&FN Spon; 1994.

RILEM, (1999) "Test for Gas Permeability of Concrete", *Materials and Structures*, **32:** 174-179

RILEM,(1999), " Concrete Durability - An Approach Towards Performance Testing" *Materials and Structures*, **32**: 163-173

RIVERA-VILLARREAL R. (1999), "Concrete superplasticizers admixtures". *Modern Concrete Materials: Binders, Additions and Admixtures,* Ed. R.K. Dhir and T.D. Dyer, Thomas Telford, London, pp.391-410

ROELS, S., ELSEN, J., et. al., (2001) "Characterization of pore structure by combining mercury porosimetry and micrography" *Materials and Structures*, **34:** 76-82

ROY D M, *The effect of blast furnace slag and related materials on the hydration and durability of concrete,* International Symposium on Durability of Concrete, 1992, pp195-208

ROY DM & IDORN G M, (1982) "Hydration, structure and properties of blast furnace slag cements, mortars and concrete" *ACI Journal* **79** (6): 444– 457.

SABIR, B. B., WILD, S., O'FARRELL, M., (1998) "A Water Sorptivity Test for Mortar and Concrete" *Materials and Structures*, **31**: 568-574

SAFIUDDIN, MD., HEARN, N., (2005) "Comparison of ASTM saturation techniques for measuring the permeable porosity of concrete" *Cement & Concrete Research*, **35**: 1008-1013

SALGUEIRO, W., A. SOMOZA, et al. (2004). "Porosity study on free mineral addition cement paste." *Cement and Concrete Research* **34**(1): 91-97.

SALKIND, N.J (200), Statistics for people who (think they) hate statistics. Sage Publications, Inc.,

SANJUAN M A & MUNOZ-MARTIALAY R (1996), "Influence of the water/cement ratio on the air permeability of concrete", *Journal of Materials Science*, **31**: 2829-2832

SANT, G., C. F. FERRARIS, et al. (2008). "Rheological properties of cement pastes: A discussion of structure formation and mechanical property development." *Cement and Concrete Research* **38**(11): 1286-1296.

SARİDEMIR, M., I. B. TOPÇU, et al. (2009). "Prediction of long-term effects of GGBFS on compressive strength of concrete by artificial neural networks and fuzzy logic." *Construction and Building Materials* **23**(3): 1279-1286.

SCRIVENER, K. L. & K. M. NEMATI (1996). "The percolation of pore space in the cement paste/aggregate interfacial zone of concrete." *Cement and Concrete Research* **26**(1): 35-40.

SEAR L (2011), UKQAA, Private communication on August 2011

SERSALE K. (1992) "Advances in Portland and blended cement". In: *Proceeding 9th International congress of the chemistry of cement*, New Delhi, India. vol. **I**;1992. p. 277–9

SHA, W. & G. B. PEREIRA (2001). "Differential scanning calorimetry study of hydrated ground granulated blast-furnace slag." *Cement and Concrete Research* **31**(2): 327-329.

SHAH S. P. (1994), Trends in the science and technology of concrete, International RILEM Workshop on Technology Transfer of the New Trends in Concrete, ConTech '94, Barcelona, November 7-9, 1994.

SHARFUDDIN AHMED, M., O. KAYALI, et al. (2008). "Chloride penetration in binary and ternary blended cement concretes as measured by two different rapid methods." *Cement and Concrete Composites* **30**(7): 576-582.

SHEHATA, M. H. & M. D. A. THOMAS (2006). "Alkali release characteristics of blended cements." *Cement and Concrete Research* **36**(6): 1166-1175.

SHI, H.-S., B.-W. XU, et al. (2009). "Influence of mineral admixtures on compressive strength, gas permeability and carbonation of high performance concrete." *Construction and Building Materials* **23**(5): 1980-1985.

SINGH, B., A. J. MAJUMDAR, et al. (1999). "Properties of BRECEM: Ten-year results." *Cement and Concrete Research* **29**(3): 429-433.

SINGH, M. & M. GARG (1995). "Activation of gypsum anhydrite-slag mixtures." *Cement and Concrete Research* **25**(2): 332-338.

SISOMONDO S., (2009), *An introduction to Science and Technology Studies: 2nd Edition*, John Wiley & Sons, London

SISOMPHON, K. & L. FRANKE (2007). "Carbonation rates of concretes containing high volume of pozzolanic materials." *Cement and Concrete Research* **37**(12): 1647-1653.

SIVASUNDARAM, V., MALHOTRA, V. M.,(1992) " Properties of Concrete Incorporating Low Quantity of Cement and High Volumes of Ground Granulated Slag" *ACI Materials Journal*, **89:** 554-563

SLEIMAN, H., A. PERROT, et al. (2010). "A new look at the measurement of cementitious paste setting by Vicat test." *Cement and Concrete Research* **40**(5): 681-686.

SONG HW & SARASWATHY V. (2006) "Studies on the corrosion resistance of reinforced steel in concrete with ground granulated blast-furnace slag – an overview" *J Hazard Mater* **138**(2):226–33

SONG, H.-W. & S.-J. KWON (2007). "Permeability characteristics of carbonated concrete considering capillary pore structure." *Cement and Concrete Research* **37**(6): 909-915.

STOEVEN P & STROEVEN M, (1999) "Assessment of packing characteristics by computer simulation, *Cement & Concrete Research,* **29:** 1201-1206

STUTZMAN, P.E., CENTENO, R.L., (1995) "Compositional Analysis of Beneficiated Fly Ashes," *National Institute of Standards and Technology* Internal Report 5598

STUTZMAN, P. (2004). "Scanning electron microscopy imaging of hydraulic cement microstructure." *Cement and Concrete Composites* **26**(8): 957-966.

SU, N., K.-C. HSU, et al. (2001). "A simple mix design method for self-compacting concrete." *Cement and Concrete Research* **31**(12): 1799-1807.

SU, N. & B. MIAO (2003). "A new method for the mix design of medium strength flowing concrete with low cement content." *Cement and Concrete Composites* **25**(2): 215-222.

SWAMY R N & BOUKNI A, (1990) "Some engineering properties of slag concrete as influenced by mix proportioning and curing", *ACI Materials Journal*, **87**, 210-220

SWAMY, R. N.(Ed) (1991), Blended Cements in Construction, Elsevier Science Publishers LTD

TAN, K., PU, X., (1998) "Strengthening effects of finely ground fly ash, granulated blast furnace slag, and their combination" *Cement & Concrete Research*, **28:** 1819-1825

TANAKA H (1983) "Property after being heated and re-hydrated of hardened cement paste", *Cement & Concrete Research*, **April :** 34-40

TANG, L. & NILSSON, L.-O. (1992), "Chloride diffusivity in high strength concrete at different ages" *Nordic Concrete Research, Publication No. 11, pp. 162-171*

TANGPAGASIT J, CHEERAROT R, JATURAPITAKKUL C & KIATTIKOMOL K, (2005) "Packing effect & pozzolanic reaction of fly ash in mortar" *Cement & Concrete Research*, **35:** 1145-1151

TASDEMIR, C, (2003) "Combined effects of mineral admixtures and curing conditions on the sorptivity coefficient of concrete" *Cement & Concrete Research*, **33**:1637-1642

TATTERSALL G H (1991), Workability and Quality Control of Concrete, E & E F Spon, London

TAYLOR, H.W.F., (1990) *Cement chemistry*, Academic Press, New York

TEYCHENNE D. C., FRANKLIN R. E. & ERNTROY, H. C. (1997) Design of normal concrete mixes, Second Edition, amended by B K Marsh, ISBN 1 86081 172 8, Building Research Establishment, 42p.

THE CONCRETE CENTRE (2009), *The Concrete Industry Sustainability Performance Report: 1st Report,* The Concrete Centre, Camberley

THOMAS M.D. & MATTHEWS J. D, (1992) "Carbonation of fly ash concrete", *Magazine of Concrete Research*, **44** (160), pp217-228

THOMAS MDA & MATTHEWS JD. (1992), "The permeability of fly ash concrete". *Mater Structures* **25**(7):388–96

THOMAS M. D. A., SHEHATA M. H., SHASHIPRAKASH S. G., HOPKINS D. S. & CAIL K. (1999), "Use of ternary cementitious systems containing silica fume and fly ash in concrete" *Cement and Concrete Research*, **29:** 1207–1214.

THOMAS, M. (2011). "The effect of supplementary cementing materials on alkali-silica reaction: A review." *Cement and Concrete Research* **41**(3): 209-216.

TOPÇU, I. B. & A. R. BOGA (2010). "Effect of ground granulate blast-furnace slag on corrosion performance of steel embedded in concrete." *Materials & Design* **31**(7): 3358-3365.

TSIVILIS, S., G. BATIS, et al. (2000). "Properties and behaviour of limestone cement concrete and mortar." *Cement and Concrete Research* **30**(10): 1679-1683

TSIVILIS, S., TSANTILAS, J., et. al., (2003) "The Permeability of Portland Limestone Cement Concrete" *Cement & Concrete Research*, **33:** 1465-1471

TSIVILIS, S., TSANTILAS, J., et. al.,(2002) Gas and water permeability of limestone cement concrete with varying limestone content - in "Innovations and Developments in Concrete Materials and Construction, Eds. Dhir, R. K. et. al.", pp 193-200

TSIVILIS, S., CHANIOTAKIS, E., et. al., (1999) "The effect of clinker and limestone quality on the gas permeability, water absorption and pore structure of limestone cement concrete" *Cement and Concrete Composites*, **21:** 139-146

TSIVILIS, S., E. CHANIOTAKIS, et al. (2002) "An analysis of the properties of Portland limestone cements and concrete." *Cement and Concrete Composites* **24**(3-4): 371-378.

TSIVILIS, S. & G. PARISSAKIS (1995). "A mathematical model for the prediction of cement strength." *Cement and Concrete Research* **25**(1): 9-14.

UCHIKAWA, H., OKAMURA, T., Binary and Ternary Components Blended Cements - in "Mineral Admixtures in Cement and Concrete, Ed. Ghosh, S. N.", 1993, pp 1-83

VITRUVIUS M.P., 2008, *An Abridgement of the Architecture of Vitruvius*, Kindle version, accessed 17th May 2011, www.amazon.com

VOGLIS, N., G. KAKALI, et al. (2005). "Portland-limestone cements. Their properties and hydration compared to those of other composite cements." *Cement and Concrete Composites* **27**(2): 191-196.

VUK, T., V. TINTA, et al. (2001). "The effects of limestone addition, clinker type and fineness on properties of Portland cement." *Cement and Concrete Research* **31**(1): 135-139.

WAINWRIGHT, P. J. & N. REY (2000). "The influence of ground granulated blastfurnace slag (GGBS) additions and time delay on the bleeding of concrete." *Cement and Concrete Composites* **22**(4): 253-257.

WAN, H., Z. SHUI, et al. (2004). "Analysis of geometric characteristics of GGBS particles and their influences on cement properties." *Cement and Concrete Research* **34**(1): 133-137.

WANG, D. & Z. CHEN (1997). "On predicting compressive strengths of mortars with ternary blends of cement, ggbfs and fly ash." *Cement and Concrete Research* **27**(4): 487-493.

WANG P Z, TRETTIN R & RUDERT V, (2005) "Effect of fineness & particle size distribution of granulated blast furnace slag on the hydraulic reactivity in the cement systems" *Advances in Cement Research*, **17**(10): 161-166

WEC (1995), "Efficient Use of Energy Utilizing High Technology: An Assessment of Energy Use in Industry and Buildings", *World Energy Council,* London

WILD, S., KHATIB, J. M., Jones, A., (1996) "Relative Strength, Pozzolanic Activity and Cement Hydration in Superplasticised Metakaolin Concrete" *Cement & Concrete Research*, **26:** 1537-1544

WILLIAMS, D. A., A. W. SAAK, et al. (1999). "The influence of mixing on the rheology of fresh cement paste." *Cement and Concrete Research* **29**(9): 1491-1496.

WIMPENNY D E, ELLIS C, PEEVES C M & HIGGINS D D, The development of strength and elastic properties in slag cement concretes under low temperature curing conditions, Proceedings of the 3rd International Conference on fly ash, silica fume, slag and natural pozzolanas in concrete, edited by Malhorta VM, Trondheim, Canada, pp 1283-1306

D.N. Winslow, S. Diamond, (1970) "A mercury porosimetry study of the evaluation of porosity in Portland cement", *J. Mater*. **5** (3) 564–585.

WONG, H. S. & H. ABDUL RAZAK (2005). "Efficiency of calcined kaolin and silica fume as cement replacement material for strength performance." *Cement and Concrete Research* **35**(4): 696-702

Wong H H & Kwan A K G, (2008), "Packing density of cementitious materials: Part 1 – Measurement using a wet packing method", *Materials and Structures,* **41: 689-701**

WORRELL, E., PRICE, L., HENDRICKS, C. & MEIDA, L. O. (2001), Carbon dioxide emissions from the global cement industry, Annual Review of Energy and Environment, LBNL-49097, Vol. 26, pp. 303–329.

WU, Z. & T. R. NAIK (2002). "Properties of concrete produced from multi=component blended cements." *Cement and Concrete Research* **32**(12): 1937-1942.

YAHIA, A., TANIMURA, M., SHIMOYAMA, Y., (2005) "Rheological properties of highly flowable mortar containing limestone filler-effect of powder content and w/c ratio" *Cement & Concrete Research*, **35:** 532-539

YEAU, K. Y. & E. K. KIM (2005). "An experimental study on corrosion resistance of concrete with ground granulate blast-furnace slag." *Cement and Concrete Research* **35**(7): 1391-1399.

YEH, I. C. (2007). "Computer-aided design for optimum concrete mixtures." *Cement and Concrete Composites* **29**(3): 193-202.

YOON, I.-S., O. ÇOPUROGLU, et al. (2007). "Effect of global climatic change on carbonation progress of concrete." *Atmospheric Environment* **41**(34): 7274-7285.

ZHANG, Y. M., W. SUN, et al. (2000). "Hydration of high-volume fly ash cement pastes." *Cement and Concrete Composites* **22**(6): 445-452.

ZHENG, JIAN JUN, LI, CHUN QING, ZHOU, XIN ZHU, (2005) "Characterization of microstructure of interfacial transition zone in concrete" *ACI Materials Journal*, **102:** 265-271

ZHENG, J. J., LI, C. Q., ZHOU, X. Z., (2005) "Thickness of interfacial transition zone and cement content profiles around aggregates" *Magazine of Concrete Research*, **57:** 397-406

ZHENG, LI, "Studies of Void Minimisation of the Solids Phases and Effects on Concrete Performance", PhD Thesis, 2001

APPENDIX A: (CHAPTER 3) SUPPLEMENTARY INFORMATION

A-1:MIX DESIGN

A-1a: CONCRETE MIX DESIGN – 100% CEM I, 0.50 w/c Ratio

MAIN PARAMETERS

W/C ratio	=	__0.5__	Aggregate type	=	Uncrushed,
Water content	=	__165__ kg/m³			20 mm max size
Nominal slump	=	___75___ mm	% <600µm (sand)	=	___54___ %

CEMENT CONTENT (Clause 5.3 of BRE mix design method)

Cement content = water content / W/C ratio

= __165__ / __0.5__ = _330_ kg/m³ →___330__ kg/m³

TOTAL AGGREGATE CONTENT (Clause 5.4, Figure 5)

For water content = ___165__ kg/m³

Relative density of 2.6 for uncrushed aggregates

gives estimated wet density of concrete = __2395__ kg/m³

Total aggregate content = wet concrete density – cement content – water content

= __2395__ - __330___ - __165___ =__1900__ kg/m³

SAND CONTENT (Clause 5.5, Figure 6)

For 20 mm max aggregate size and 75 nominal slump, with

w/c ratio __0.5__ and __54__ % sand < 600 µm, proportion of sand = ___40___ %

Sand content = total aggregate content × (proportion of sand / 100)

= __1900__ x (__40__ / 100)

= __760__ kg/m³ →___760__ kg/m³

10 + 20 mm AGGREGATE

Coarse aggregate content = Total aggregate content – Sand content

= __1900__ - __760___ →__1140__ kg/m³

10 mm AGGREGATE

Combine 10 and 20 mm aggregate in ratio 1:2

10 mm aggregate = Coarse aggregate content / 3

= __1140__ / 3 →___380__ kg/m³

20 mm AGGREGATE

20 mm aggregate = Coarse aggregate content – 10 mm aggregate content

= __1140__ - ___380__→__760___ kg/m³

After determining the mix proportions using the BRE method, following steps were taken:

- **Correction for concrete yield, based on the particle densities (at SSD for aggregates) of the mix constituents, with no allowance made for entrapped air (therefore slight over-yield).**
- **Calculation of batch quantities, with water content increased and aggregate content reduced to allow for water absorption by the aggregates from laboratory-dry to SSD.**
- **Measurement of plastic density as an approximate check on mix design and batching.**

A-1b: CONCRETE MIX DESIGN – 45% CEM I + 45% GGBS + 10% Fly Ash, 0.50 w/c Ratio

MAIN PARAMETERS

W/C ratio	=	__0.5__	Aggregate type	=	Uncrushed,
Water content	=	__165__ kg/m³			20 mm max size
Nominal slump	=	___75___ mm	% <600µm (sand)	=	___54___ %

CEMENT CONTENT (Clause 5.3 of BRE mix design method)

Cement content	=	water content / W/C ratio		
	=	__165__ / __0.5__=	_330_ kg/m³→	___330__ kg/m³
CEM I content	=	__330__ × _0.45__=	148.5 kg/m³→	___149__ kg/m³
GGBS content	=	__330__ × _0.45__=	148.5 kg/m³→	___148__ kg/m³
Fly Ash content	=	__330__ × _0.10__=	__33_ kg/m³→	____33__ kg/m³

TOTAL AGGREGATE CONTENT (Clause 5.4, Figure 5)

For water content		=	___165__ kg/m³
Relative density of 2.6 for uncrushed aggregates			
gives estimated wet density of concrete		=	__2395__ kg/m³
Total aggregate content	=	wet concrete density – cement content – water content	
	=	__2395__ - __330___ - __165___=	__1900__ kg/m³

SAND CONTENT (Clause 5.5, Figure 6)

For 20 mm max aggregate size and 75 nominal slump, with
w/c ratio __0.5__ and __54__ % sand < 600 µm, proportion of sand =___40___ %

Sand content	=	total aggregate content × (proportion of sand / 100)	
	=	__1900__ x (__40__ / 100)	
	=	__760__ kg/m³	→___760__ kg/m³

10 + 20 mm AGGREGATE

Coarse aggregate content	=	Total aggregate content – Sand content	
	=	__1900__ - __760___ →	__1140__ kg/m³

10 mm AGGREGATE

Combine 10 and 20 mm aggregate in ratio 1:2

10 mm aggregate	=	Coarse aggregate content / 3	
	=	__1140__ / 3 →	___380__ kg/m³

20 mm AGGREGATE

20 mm aggregate	=	Coarse aggregate content – 10 mm aggregate content	
	=	__1140__ - ___380__→	__760___ kg/m³

After determining the mix proportions using the BRE method, following steps were taken:

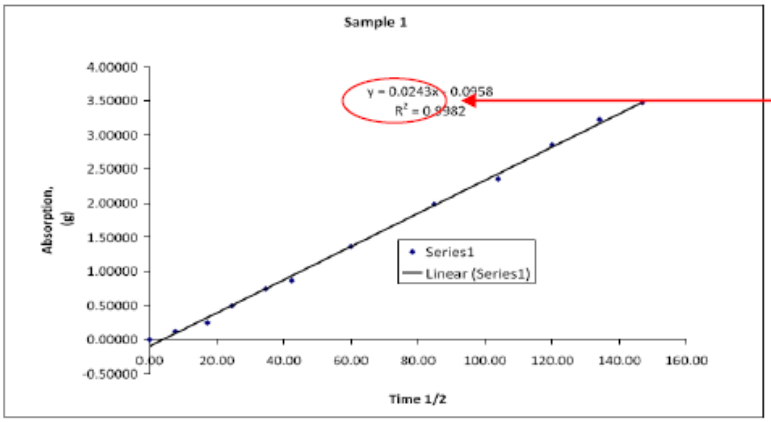
- **Correction for concrete yield, based on the particle densities (at SSD for aggregates) of the mix constituents, with no allowance made for entrapped air (therefore slight over-yield).**
- **Calculation of batch quantities, with water content increased and aggregate content reduced to allow for water absorption by the aggregates from laboratory-dry to SSD.**
- **Measurement of plastic density as an approximate check on mix design and batching.**

A-2: Sorptivity Calculation Datasheet

Diameter:	101	100	100			
	Av. Diameter		100.33 mm			
Thickness:	50	52	50	Mass after Sealing Specimen:		
	Av. Thickness		50.7 mm		957	
Water Temperature:				Exposed Area:	7906.4	

Test Time			Time $^{1/2}$	Mass	Change in Mass	Absorption
Days	Min	Seconds		g	g	g
		0	0.00	957	0	0.00000
	1	60	7.75	958	1.00	0.12408
	5	300	17.32	959	2.00	0.24815
	10	600	24.49	961	4.00	0.49631
	20	1200	34.64	963	6.00	0.74446
	30	1800	42.43	964	7.00	0.86853
	60	3600	60.00	968	11.00	1.36484
	120	7200	84.85	973	16.00	1.98522
	180	10800	103.92	976	19.00	2.35745
	240	14400	120.00	980	23.00	2.85376
	300	18000	134.16	983	26.00	3.22599
	360	21600	146.97	985	28.00	3.47414
1.07	1537	92220	303.68	1011	54.00	6.70012
2.24	3220	193200	439.55	1013.57	56.57	7.01900
3.11	4475	268500	518.17	1013.95	56.95	7.06615
5.00	7200	432000	657.27	1014.19	57.19	7.09593
6.11	8793	527580	726.35	1014.41	57.41	7.12322
7.20	10370	622200	788.80	1014.54	57.54	7.13935
8.00	11520	691200	831.38	1014.71	57.71	7.16045

Data form the sorptivity test (the measured weight at each timed interval) is entered into the yellow cells and the Y & X Axis are calculated automatically and plotted on the chart.



The absorption coefficient is taken from the "y" intercept line on the chart.

A-3: Air Permeability Calculation Datasheet

100% PC

Diameter	54	54	54
Average Diameter	54 mm		
Cross Sectional Area, A =	0.00229 m^2		
Length	52	51	54
Average Length, L	0.052	m	

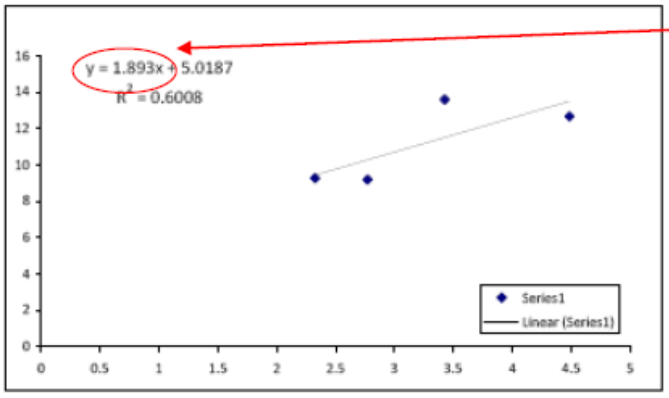
P_1 (Pa)	$P_{1\,(psi)}$	Q_2	Q_2
758620.6897	110	38	6.33E-07
620689.6552	90	25	4.17E-07
482758.6207	70	22	3.67E-07
344827.5862	50	10	1.67E-07
206896.5517	30	7	1.17E-07

m =	Dynamic viscosity of air =	1.79E-05
P_2 =	Outlet Pressure (Atmos) =	101000

	Y-Axis	X-AXIS 1/Pm
k_1	9.257577023	2.32660757
k_2	9.179975498	2.77127431
k_3	13.59554389	3.4260736
k_4	12.6691153	4.48603914
k_5	29.56701365	6.49568821

Intercept from graph

Intrinsic Permeability (k)= 1.893



Data is entered into the yellow cells and the Y & X Axis are calculated automatically and plotted on the chart.

The intrinsic air permeability is taken from the "y" intercept line on the chart.

A-4: ECO2 Data

A-4a: 0.35 w/c ratio

Mix No	Aggregates					ECO2							ECO2
	PC	GGBS	PFA	LS	Sand	5-10 mm	10-20 mm	PC	GGBS	PFA	LS	Water	Aggs	(kg/m3)
1a	478	-	-	-	606	392	785	444.54	-	-	-	0.495	7.132	452
2a	309	167	-	-	604	391	782	287.37	8.684	-	-	0.495	7.108	304
3a	309	122	45	-	604	391	782	287.37	6.344	0.18	-	0.495	7.108	301
4a	309	122	-	47	604	391	782	287.37	6.344	-	1.504	0.495	7.108	303
5a	214	261	-	-	603	390	780	199.02	13.572	-	-	0.495	7.092	220
6a	214	213	45	-	635	389	780	199.02	11.076	0.18	-	0.495	7.216	218
7a	214	165	90	-	635	389	780	199.02	8.58	0.36	-	0.495	7.216	216
8a	213	213	-	47	601	388	779	198.09	11.076	-	1.504	0.495	7.072	218
9a	214	165	-	90	635	388	779	199.02	8.58	-	2.88	0.495	7.208	218
10a	119	355	-	-	630	389	779	110.67	18.46	-	-	0.495	7.192	137
11a	120	305	50	-	630	388	778	111.6	15.86	0.2	-	0.495	7.184	135
12a	120	255	95	-	630	388	778	111.6	13.26	0.38	-	0.495	7.184	133
13a	120	305	-	50	630	387	778	111.6	15.86	-	1.6	0.495	7.18	137
14a	120	255	-	95	630	387	778	111.6	13.26	-	3.04	0.495	7.18	136
15a	120	190	-	165	625	388	778	111.6	9.88	-	5.28	0.495	7.164	134

A-4b: 0.5 w/c ratio

Mix No	Binder (kg/m3)				Aggregates (kg/m3)			ECO2 (kg/m3)					ECO2 (kg/m3)
	PC	GGBS	PFA	LS	Sand	5-10 mm	10-20 mm	PC	GGBS	PFA	LS	Water	Aggs	
1b	333	-	-	-	655	417	833	309.69	-	-	-	0.495	7.62	318
2b	216	116	-	-	651	414	823	200.88	6.032	-	-	0.495	7.552	215
3b	215	80	33	-	651	414	823	199.95	4.16	0.132	-	0.495	7.552	212
4b	215	80	-	33	651	414	823	199.95	4.16	-	1.056	0.495	7.552	213
5b	150	182	-	-	650	413	826	139.5	9.464	-	-	0.495	7.556	157
6b	150	150	33	-	650	413	826	139.5	7.8	0.132	-	0.495	7.556	155
7b	150	115	65	-	650	413	826	139.5	5.98	0.26	-	0.495	7.556	154
8b	150	150	-	33	650	413	826	139.5	7.8	-	1.056	0.495	7.556	156
9b	150	115	-	60	650	412	825	139.5	5.98	-	1.92	0.495	7.548	155
10b	83	250	-	-	649	413	825	77.19	13	-	-	0.495	7.548	98
11b	83	215	33	-	649	413	825	77.19	11.18	0.132	-	0.495	7.548	97
12b	83	182	70	-	649	413	825	77.19	9.464	0.28	-	0.495	7.548	95
13b	83	215	-	33	649	411	822	77.19	11.18	-	1.056	0.495	7.528	97
14b	83	182	-	70	649	411	822	77.19	9.464	-	2.24	0.495	7.528	97
15b	83	130	-	120	646	411	822	77.19	6.76	-	3.84	0.495	7.516	96

A-4c: 0.65 w/c ratio

Mix No	PC	GGBS	PFA	LS	Aggregates			ECO2						ECO2
					Sand	5-10 mm	10-20 mm	PC	GGBS	PFA	LS	Water	Aggs	(kg/m3)
1c	256	-	-	-	685	430	859	238.08	-	-	-	0.495	7.896	246
2c	165	90	-	-	683	429	857	153.45	4.68	-	-	0.495	7.876	167
3c	165	65	25	-	683	429	857	153.45	3.38	0.1	-	0.495	7.876	165
4c	165	65	-	25	683	429	857	153.45	3.38	-	0.8	0.495	7.876	166
5c	115	140	-	-	683	428	857	106.95	7.28	-	-	0.495	7.872	123
6c	115	115	25	-	683	428	857	106.95	5.98	0.1	-	0.495	7.872	121
7c	115	90	50	-	683	428	857	106.95	4.68	0.2	-	0.495	7.872	120
8c	115	115	-	25	682	428	854	106.95	5.98	-	0.8	0.495	7.856	122
9c	115	90	-	50	682	428	854	106.95	4.68	-	1.6	0.495	7.856	122
10c	65	190	-	-	682	427	856	60.45	9.88	-	-	0.495	7.86	79
11c	65	165	25	-	682	427	856	60.45	8.58	0.1	-	0.495	7.86	77
12c	65	140	50	-	682	427	856	60.45	7.28	0.2	-	0.495	7.86	76
13c	65	165	-	25	680	426	856	60.45	8.58	-	0.8	0.495	7.848	78
14c	65	140	-	50	680	426	854	60.45	7.28	-	1.6	0.495	7.84	78
15c	65	100	-	90	680	426	854	60.45	5.2	-	2.88	0.495	7.84	77

A-5: Curve Fitting Procedure

STEP 1

Plot the strength compressive strengths against w/c ratio, test age and cement combination content. As there were two measurements taken at each test age two data points are available. Thereafter based on the raw data the line of best fit was drawn to the data points. These are drawing so that smooth parallel curves are obtained and ideally these lines should pass through the centre of the original data points. Although this was possible to a certain extent, there were instances where this was not achieved for all the data sets when maintaining a smooth curve. It was however generally possible for the data points to pass through or between the highest and lowest data points. Where this was not possible the lines were drawing as close as possible to these original data points. Figure A.1 demonstrates the first stage in the curve fitting procedure where strength is plotted against w/c ratio.

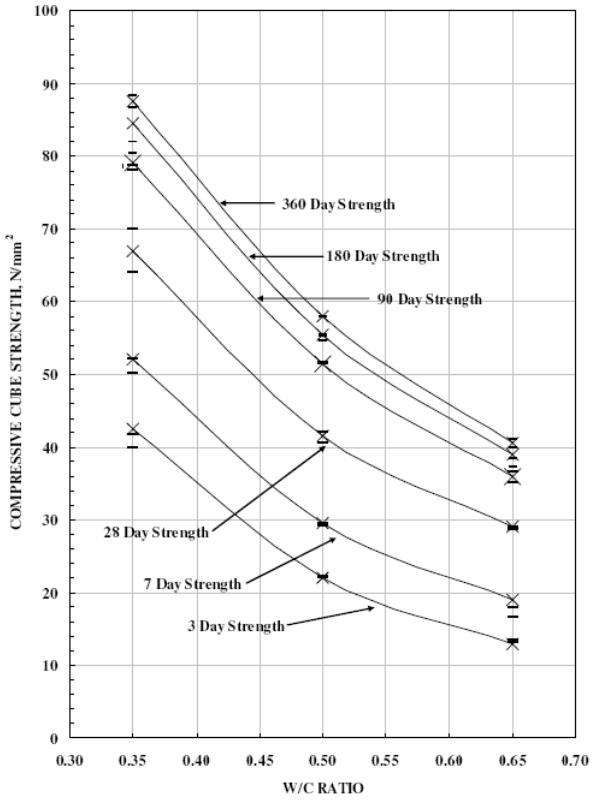


Fig A.1: Compressive strength normalisation

STEP 2 and STEP 3

The data from Step One was then plotted on a compressive strength against time (step 2) and thirdly compressive strength against log time graph (step 3). These data points were plotted along with the original raw data points in all cases as can be seen in Figure A2 (a) and (b).

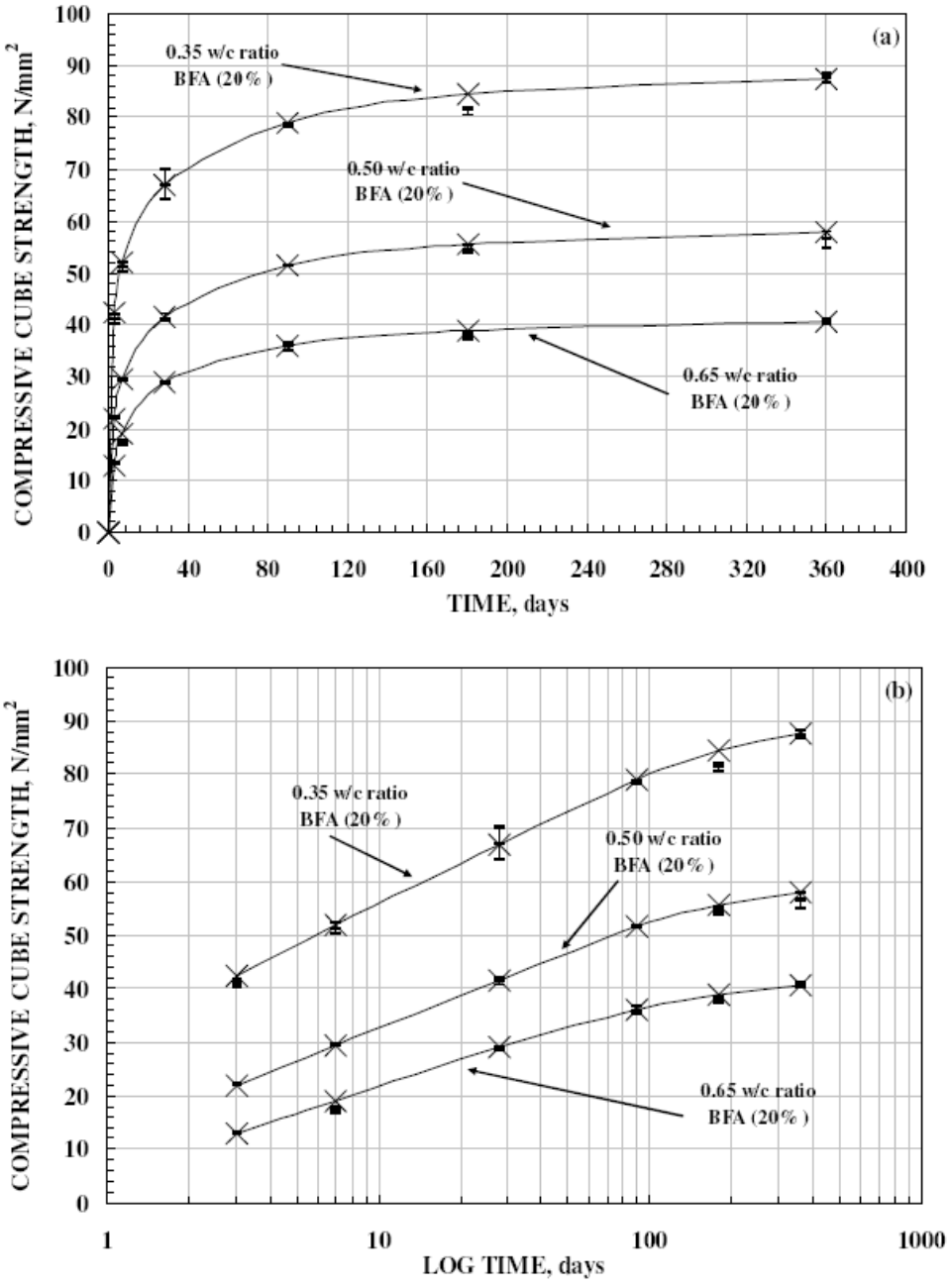


Fig A.2: Compressive Strength normalisation with (a) time and (b) log time

STEP 4

As the outcome of Steps One, Two and Three was to obtain smooth curves representative of the raw test data an iterative procedure was followed. This was necessary to ensure that the final data obtained was representative of the original test data and as such required the procedure to be undertaken a number of times.

STEP 5

Thereafter with respect to the data obtained from the remaining test methods this strength data was applied in facilitating a fifth step in the curve fitting procedure. Although no graph is presented in this demonstration it can be seen from Table B.9 that this was undertaken for five of the data sets in total.

APPENDIX B: (CHAPTER 4) SUPPLEMENTARY INFORMATION

B-1: Viscometry & Setting Time

Viscometry

Mix Combination	Plastic Viscosity ($kgm^{-1}s^{-1}$)	Yield Stress (N/mm^2)
CEM I	0.687	0.21
65%PC + 35%GGBS	0.437	0.34
65%PC + 25%GGBS + 10%FA	0.388	0.37
65%PC + 25%GGBS + 10%LS	0.445	0.4
45%PC + 55% GGBS	0.309	0.41
45%PC + 45%GGBS + 10%FA	0.351	0.48
45%PC + 45%GGBS + 10%LS	0.351	0.5
25%PC + 75%GGBS	0.318	0.33
25%PC + 65%GGBS + 10%FA	0.287	0.4
25%PC + 55%GGBS + 20%FA	0.365	0.5
25%PC + 65%GGBS + 10%LS	0.276	0.45
25%PC + 55%GGBS + 20%LS	0.386	0.52

Setting Time

Mix Combination	Start	Finish
0.35 w/c ratio		
CEM I	01:41:48	02:34:44
65%PC + 35%GGBS	01:42:15	03:37:21
65%PC + 25%GGBS + 10%FA	01:52:18	02:38:17
65%PC + 25%GGBS + 10%LS	01:50:53	02:31:00
45%PC + 55% GGBS	02:02:03	04:13:58
45%PC + 45%GGBS + 10%FA	02:08:39	03:10:12
45%PC + 45%GGBS + 10%LS	01:52:02	02:53:16
25%PC + 75%GGBS	02:50:09	03:41:00
25%PC + 65%GGBS + 10%FA	01:59:01	03:23:00
0.5 w/c ratio		
CEM I	03:53:47	05:13:34
65%PC + 35%GGBS	03:40:55	06:30:04
65%PC + 25%GGBS + 10%FA	02:56:01	07:27:35
65%PC + 25%GGBS + 10%LS	03:19:24	04:11:12
45%PC + 55% GGBS	03:55:46	04:56:42
45%PC + 45%GGBS + 10%FA	03:48:41	06:00:38
45%PC + 45%GGBS + 10%LS	01:51:49	06:28:47
25%PC + 75%GGBS	02:43:32	08:07:08
25%PC + 65%GGBS + 10%FA	00:56:04	05:49:45

B-2: Packing Density, Void ratio and Standard Consistency

Mix Combination	Packing Denisty	Void Ratio	% water
CEM I	53.33	0.53	31.8
65%PC + 35%GGBS	60.21	0.60	28.6
65%PC + 25%GGBS + 10%FA	55.62	0.56	29.6
65%PC + 25%GGBS + 10%LS	54.44	0.54	28.4
45%PC + 55% GGBS	61.66	0.62	30.2
45%PC + 45%GGBS + 10%FA	57.96	0.58	31.2
45%PC + 35%GGBS + 20%FA	51.80	0.52	31.6
45%PC + 45%GGBS + 10%LS	57.11	0.57	30.2
45%PC + 35%GGBS + 20%LS	51.47	0.51	30
25%PC + 75%GGBS	66.39	0.66	30.8
25%PC + 65%GGBS + 10%FA	57.65	0.58	31.6
25%PC + 55%GGBS + 20%FA	52.05	0.52	31.4
25%PC + 65%GGBS + 10%LS	61.09	0.61	30.8
25%PC + 55%GGBS + 20%LS	56.89	0.57	30.6
25%PC + 40%GGBS + 35%LS	48.31	0.48	30.8

B-3: Strength

Mix Combination	Compressive Strength (N/mm²) test age				
	3	7	28	90	120
0.35 w/c ratio					
CEM I	44	47	48	56	60
65%PC + 35%GGBS	28	35	41	50	55
65%PC + 25%GGBS + 10%FA	31	34	39	48	53.5
65%PC + 25%GGBS + 10%LS	34	37	43	55	59.5
45%PC + 55% GGBS	32	36	42	56	64.5
45%PC + 45%GGBS + 10%FA	31	37	41	50	53.5
45%PC + 45%GGBS + 10%LS	31	34	37	48	53
25%PC + 75%GGBS	27	30	35	44	48.5
25%PC + 65%GGBS + 10%FA	25	33	36	48	52
25%PC + 65%GGBS + 10%LS	27	34	37	46	50.5
0.5 w/c ratio					
CEM I	18	20	23	30	34
65%PC + 35%GGBS	10	20	25	36	43
65%PC + 25%GGBS + 10%FA	11	17	21	29	34
65%PC + 25%GGBS + 10%LS	12	17	22	34	38
45%PC + 55% GGBS	9	13	17	34	39.5
45%PC + 45%GGBS + 10%FA	8	14	19	27	31
45%PC + 45%GGBS + 10%LS	6	13	18	28	34
25%PC + 75%GGBS	9	11	15	24	28.5
25%PC + 65%GGBS + 10%FA	5	13	17	28	33
25%PC + 65%GGBS + 10%LS	6	13	16	26	29.5

APPENDIX C: (CHAPTER 5) SUPPLEMENTARY INFORMATION

C-1: Compressive Strength

Mix Combination	Compressive Strength (N/mm^2) test age				
	3	7	28	90	180
0.35 w/c ratio					
CEM I	50	60	70	78	82
65%PC + 35%GGBS	36	50	69	79	84
65%PC + 25%GGBS + 10%FA	30	35	52	60	65
65%PC + 25%GGBS + 10%LS	25	37	55	64	69
45%PC + 55% GGBS	28	40	59	73	78
45%PC + 45%GGBS + 10%FA	29	41	57	64	70
45%PC + 35%GGBS + 20%FA	21	32	52	58	61
45%PC + 45%GGBS + 10%LS	24	37	53	63	68
45%PC + 35%GGBS + 20%LS	26	37	51	58	62
25%PC + 75%GGBS	21	31	47	59	65
25%PC + 65%GGBS + 10%FA	29	35	49	56	61
25%PC + 55%GGBS + 20%FA	24	37	50	58	65
25%PC + 65%GGBS + 10%LS	17	23	32	36	41
25%PC + 55%GGBS + 20%LS	26	33	43	49	53
25%PC + 40%GGBS + 35%LS	17	23	33	38	44
0.5 w/c ratio					
CEM I	28	38	48	53	56
65%PC + 35%GGBS	20	31	47	55	59
65%PC + 25%GGBS + 10%FA	18	27	42	51	54
65%PC + 25%GGBS + 10%LS	16	27	43	52	56
45%PC + 55% GGBS	16	25	39	51	58
45%PC + 45%GGBS + 10%FA	13	25	44	50	56
45%PC + 35%GGBS + 20%FA	13	23	38	47	49
45%PC + 45%GGBS + 10%LS	13	26	40	50	54
45%PC + 35%GGBS + 20%LS	12	23	37	45	50
25%PC + 75%GGBS	11	19	30	38	44
25%PC + 65%GGBS + 10%FA	16	21	34	40	44
25%PC + 55%GGBS + 20%FA	11	19	32	39	46
25%PC + 65%GGBS + 10%LS	10	15	22	25	29
25%PC + 55%GGBS + 20%LS	11	18	28	36	40
25%PC + 40%GGBS + 35%LS	7	13	23	29	33
0.65 w/c ratio					
CEM I	15	23	34	38	40
65%PC + 35%GGBS	13	21	33	40	43
65%PC + 25%GGBS + 10%FA	10	19	35	42	48
65%PC + 25%GGBS + 10%LS	10	19	32	40	44
45%PC + 55% GGBS	10	19	29	38	41
45%PC + 45%GGBS + 10%FA	9	20	36	42	48
45%PC + 35%GGBS + 20%FA	11	17	30	39	43
45%PC + 45%GGBS + 10%LS	7	18	31	40	45
45%PC + 35%GGBS + 20%LS	6	15	28	35	39
25%PC + 75%GGBS	6	13	23	31	36
25%PC + 65%GGBS + 10%FA	7	12	26	31	35
25%PC + 55%GGBS + 20%FA	5	12	22	30	37
25%PC + 65%GGBS + 10%LS	3	9	15	19	23
25%PC + 55%GGBS + 20%LS	4	11	21	28	33
25%PC + 40%GGBS + 35%LS	4	9	18	25	28

C-2: Cementing Efficiency Relative to CEM I concrete

Mix Combination	Cement efficiency relative to CEM I (1.0)				
	3	7	28	90	180
0.35 w/c ratio					
65%PC + 35%GGBS	0.73	0.96	1.01	1.04	1.06
65%PC + 25%GGBS + 10%FA	0.60	0.66	0.77	0.80	0.82
65%PC + 25%GGBS + 10%LS	0.49	0.71	0.77	0.79	0.84
45%PC + 55% GGBS	0.57	0.77	0.77	0.80	0.85
45%PC + 45%GGBS + 10%FA	0.59	0.79	0.83	0.84	0.89
45%PC + 35%GGBS + 20%FA	0.42	0.60	0.73	0.76	0.76
45%PC + 45%GGBS + 10%LS	0.47	0.71	0.82	0.84	0.87
45%PC + 35%GGBS + 20%LS	0.53	0.71	0.74	0.77	0.81
25%PC + 75%GGBS	0.42	0.58	0.69	0.79	0.85
25%PC + 65%GGBS + 10%FA	0.59	0.67	0.72	0.72	0.76
25%PC + 55%GGBS + 20%FA	0.48	0.71	0.72	0.77	0.82
25%PC + 65%GGBS + 10%LS	0.34	0.44	0.47	0.47	0.52
25%PC + 55%GGBS + 20%LS	0.52	0.63	0.63	0.64	0.66
25%PC + 40%GGBS + 35%LS	0.34	0.44	0.48	0.48	0.52
0.5 w/c ratio					
65%PC + 35%GGBS	0.08	0.10	1.00	1.02	1.03
65%PC + 25%GGBS + 10%FA	0.07	0.08	0.93	0.92	0.95
65%PC + 25%GGBS + 10%LS	0.06	0.08	0.89	0.87	0.89
45%PC + 55% GGBS	0.06	0.08	0.93	0.92	0.98
45%PC + 45%GGBS + 10%FA	0.05	0.08	0.98	0.92	0.98
45%PC + 35%GGBS + 20%FA	0.05	0.07	0.85	0.81	0.86
45%PC + 45%GGBS + 10%LS	0.05	0.08	1.00	0.94	0.96
45%PC + 35%GGBS + 20%LS	0.05	0.07	0.82	0.76	0.86
25%PC + 75%GGBS	0.04	0.06	0.67	0.78	0.86
25%PC + 65%GGBS + 10%FA	0.06	0.06	0.74	0.72	0.75
25%PC + 55%GGBS + 20%FA	0.04	0.06	0.69	0.72	0.81
25%PC + 65%GGBS + 10%LS	0.04	0.05	0.49	0.46	0.51
25%PC + 55%GGBS + 20%LS	0.04	0.06	0.63	0.66	0.72
25%PC + 40%GGBS + 35%LS	0.03	0.04	0.50	0.54	0.58
0.65 w/c ratio					
65%PC + 35%GGBS	1.82	1.40	1.06	1.17	1.16
65%PC + 25%GGBS + 10%FA	1.45	1.23	1.20	1.20	1.21
65%PC + 25%GGBS + 10%LS	1.45	1.26	1.10	1.14	1.16
45%PC + 55% GGBS	1.45	1.23	1.20	1.26	1.29
45%PC + 45%GGBS + 10%FA	1.31	1.33	1.24	1.20	1.23
45%PC + 35%GGBS + 20%FA	1.53	1.13	1.06	1.12	1.05
45%PC + 45%GGBS + 10%LS	1.02	1.20	1.27	1.23	1.26
45%PC + 35%GGBS + 20%LS	0.87	0.96	0.96	0.89	1.00
25%PC + 75%GGBS	0.87	0.83	0.68	0.89	0.98
25%PC + 65%GGBS + 10%FA	1.02	0.80	0.86	0.86	0.90
25%PC + 55%GGBS + 20%FA	0.73	0.80	0.68	0.83	0.98
25%PC + 65%GGBS + 10%LS	0.44	0.60	0.52	0.54	0.59
25%PC + 55%GGBS + 20%LS	0.58	0.73	0.70	0.79	0.84
25%PC + 40%GGBS + 35%LS	0.51	0.60	0.65	0.70	0.73

C-3: Total Porosity & Critical Pore Size

Mix Combination	Total Porosity(%)			
	3	7	28	180
0.35 w/c ratio				
CEM I	25	24	22	17.2
65%PC + 35%GGBS	29	25	20.5	15.5
65%PC + 25%GGBS + 10%FA	31	27	20	14
65%PC + 25%GGBS + 10%LS	32	27	20.5	17.5
45%PC + 55% GGBS	32	26	21	15
45%PC + 45%GGBS + 10%FA	29	25	20.5	15
45%PC + 45%GGBS + 10%LS	27	24	22	19
0.5 w/c ratio				
CEM I	31	28	24	21
65%PC + 35%GGBS	30	27	23	19.5
65%PC + 25%GGBS + 10%FA	33	28	23	20.5
65%PC + 25%GGBS + 10%LS	34	28	23.5	20
45%PC + 55% GGBS	35	28	23.5	20.3
45%PC + 45%GGBS + 10%FA	30	27	23.5	20.5
45%PC + 45%GGBS + 10%LS	29	25	23	21

Mix Combination	Critical Pore Size (µm)			
	3	7	28	180
0.35 w/c ratio				
CEM I	0.27	0.17	0.1	0.09
65%PC + 35%GGBS	0.17	0.13	0.09	0.06
65%PC + 25%GGBS + 10%FA	0.23	0.19	0.1	0.07
65%PC + 25%GGBS + 10%LS	0.19	0.16	0.07	0.06
45%PC + 55% GGBS	0.3	0.24	0.19	0.14
45%PC + 45%GGBS + 10%FA	0.27	0.2	0.17	0.11
45%PC + 45%GGBS + 10%LS	0.23	0.19	0.16	0.11
0.5 w/c ratio				
CEM I	0.4	0.2	0.17	0.13
65%PC + 35%GGBS	0.21	0.2	0.14	0.11
65%PC + 25%GGBS + 10%FA	0.37	0.33	0.16	0.12
65%PC + 25%GGBS + 10%LS	0.23	0.19	0.11	0.1
45%PC + 55% GGBS	0.56	0.37	0.29	0.24
45%PC + 45%GGBS + 10%FA	0.31	0.29	0.23	0.19
45%PC + 45%GGBS + 10%LS	0.27	0.24	0.21	0.13

APPENDIX D: (CHAPTER 6) SUPPLEMENTARY INFORMATION

D-1 ISAT & Sorptivity

D-2 Paste Sorptivity

D-1: ISAT & Sorptivity

Mix Combination	ISAT-10 x10^{-2} ml/m^2,s		Sorptivity x10^{-4},mm/√s	
	28	180	28	180
0.35 w/c ratio				
CEM I	31	25	195	155
65%PC + 35%GGBS	29	21	180	130
65%PC + 25%GGBS + 10%FA	34	30	210	140
65%PC + 25%GGBS + 10%LS	32	23	185	135
45%PC + 55% GGBS	30	24	185	135
45%PC + 45%GGBS + 10%FA	41	27	245	150
45%PC + 35%GGBS + 20%FA	44	28	225	155
45%PC + 45%GGBS + 10%LS	36	29	190	145
45%PC + 35%GGBS + 20%LS	38	27	210	120
25%PC + 75%GGBS	40	31	220	165
25%PC + 65%GGBS + 10%FA	52	33	220	175
25%PC + 55%GGBS + 20%FA	58	34	210	175
25%PC + 65%GGBS + 10%LS	45	24	215	160
25%PC + 55%GGBS + 20%LS	49	35	230	150
25%PC + 40%GGBS + 35%LS	52	37	260	160
0.5 w/c ratio				
CEM I	47	38	270	225
65%PC + 35%GGBS	44	31	245	185
65%PC + 25%GGBS + 10%FA	42	30	270	175
65%PC + 25%GGBS + 10%LS	42	32	255	185
45%PC + 55% GGBS	45	34	255	190
45%PC + 45%GGBS + 10%FA	53	31	310	190
45%PC + 35%GGBS + 20%FA	54	33	285	200
45%PC + 45%GGBS + 10%LS	50	38	260	197
45%PC + 35%GGBS + 20%LS	52	36	275	190
25%PC + 75%GGBS	54	40	320	230
25%PC + 65%GGBS + 10%FA	68	39	275	220
25%PC + 55%GGBS + 20%FA	69	42	260	220
25%PC + 65%GGBS + 10%LS	59	49	290	210
25%PC + 55%GGBS + 20%LS	63	45	310	220
25%PC + 40%GGBS + 35%LS	65	50	320	227
0.65 w/c ratio				
CEM I	69	57	380	325
65%PC + 35%GGBS	62	46	330	265
65%PC + 25%GGBS + 10%FA	55	44	340	220
65%PC + 25%GGBS + 10%LS	60	45	335	260
45%PC + 55% GGBS	63	46	350	260
45%PC + 45%GGBS + 10%FA	73	48	390	240
45%PC + 35%GGBS + 20%FA	67	46	360	250
45%PC + 45%GGBS + 10%LS	67	50	340	275
45%PC + 35%GGBS + 20%LS	72	48	355	270
25%PC + 75%GGBS	71	52	450	320
25%PC + 65%GGBS + 10%FA	69	61	350	270
25%PC + 55%GGBS + 20%FA	79	67	320	270
25%PC + 65%GGBS + 10%LS	77	53	315	245
25%PC + 55%GGBS + 20%LS	81	57	395	310
25%PC + 40%GGBS + 35%LS	86	69	400	330

D-2: Paste Sorptivity

Mix Combinations	Sorptivity $x10^{-4}$,mm/√s
0.35 w/c ratio	
CEM I	791
65%PC + 35%GGBS	725
65%PC + 25%GGBS + 10%PFA	805
65%PC + 25%GGBS + 10%LS	925
45%PC + 55% GGBS	993
45%PC + 45%GGBS + 10%PFA	975
45%PC + 45%GGBS + 10%LS	1095
25%PC + 75%GGBS	1250
25%PC + 65%GGBS + 10%FA	1020
25%PC + 65%GGBS + 10%LS	1897
0.5 w/c ratio	
CEM I	1103
65%PC + 35%GGBS	1028
65%PC + 25%GGBS + 10%PFA	1098
65%PC + 25%GGBS + 10%LS	1315
45%PC + 55% GGBS	1427
45%PC + 45%GGBS + 10%PFA	1269
45%PC + 45%GGBS + 10%LS	1521
25%PC + 75%GGBS	1900
25%PC + 65%GGBS + 10%FA	1327
25%PC + 65%GGBS + 10%LS	2547

APPENDIX E: (CHAPTER 7) SUPPLEMENTARY INFORMATION

E-1 Air Permeability

E-2 Water Penetration Under Pressure

E-1: Air Permeability

Mix Combination	Air Permeability ($x10^{-17}$),m^2	
	28	180
0.35 w/c ratio		
CEM I	1.7	1.4
65%PC + 35%GGBS	1.8	1
65%PC + 25%GGBS + 10%FA	2.4	1.4
65%PC + 25%GGBS + 10%LS	1.7	1.4
45%PC + 55% GGBS	3.1	2.5
45%PC + 45%GGBS + 10%FA	3.9	3
45%PC + 35%GGBS + 20%FA	4.3	3.4
45%PC + 45%GGBS + 10%LS	2.5	2.8
45%PC + 35%GGBS + 20%LS	3.5	3.3
25%PC + 75%GGBS	7.1	6.1
25%PC + 65%GGBS + 10%FA	8.6	6.6
25%PC + 55%GGBS + 20%FA	9.2	7.2
25%PC + 55%GGBS + 20%LS	7.7	6.9
25%PC + 40%GGBS + 35%LS	9	7.7
0.5 w/c ratio		
CEM I	2.5	2.2
65%PC + 35%GGBS	3	2
65%PC + 25%GGBS + 10%FA	4.1	2.4
65%PC + 25%GGBS + 10%LS	2	1.7
45%PC + 55% GGBS	5.7	4.5
45%PC + 45%GGBS + 10%FA	7.2	4.8
45%PC + 35%GGBS + 20%FA	7.8	5.1
45%PC + 45%GGBS + 10%LS	4	3.9
45%PC + 35%GGBS + 20%LS	5	4.9
25%PC + 75%GGBS	11.9	10
25%PC + 65%GGBS + 10%FA	14	10.3
25%PC + 55%GGBS + 20%FA	14.7	10.9
25%PC + 55%GGBS + 20%LS	10.9	10.7
25%PC + 40%GGBS + 35%LS	12.6	11.1
0.65 w/c ratio		
CEM I	4.7	3.9
65%PC + 35%GGBS	5.8	3.8
65%PC + 25%GGBS + 10%FA	7.2	3.6
65%PC + 25%GGBS + 10%LS	3.4	2.9
45%PC + 55% GGBS	9.7	7.6
45%PC + 45%GGBS + 10%FA	11.6	7.3
45%PC + 35%GGBS + 20%FA	12.2	8.1
45%PC + 45%GGBS + 10%LS	6.6	6.1
45%PC + 35%GGBS + 20%LS	8.1	7.3
25%PC + 75%GGBS	19	15
25%PC + 65%GGBS + 10%FA	21.9	14.6
25%PC + 55%GGBS + 20%FA	21.9	14.6
25%PC + 55%GGBS + 20%LS	15.5	14.6
25%PC + 40%GGBS + 35%LS	18.3	15.4

E-2: Water Penetration Under Pressure

Mix Combination	Water Penetration mm	
	28	180
0.35 w/c ratio		
CEM I	10	7
65%PC + 35%GGBS	9	5
65%PC + 25%GGBS + 10%FA	12	6
65%PC + 25%GGBS + 10%LS	14	6
45%PC + 55% GGBS	14	7
45%PC + 45%GGBS + 10%FA	20	9
45%PC + 35%GGBS + 20%FA	24	10
45%PC + 45%GGBS + 10%LS	23	10
45%PC + 35%GGBS + 20%LS	30	12
25%PC + 75%GGBS	25	12
25%PC + 65%GGBS + 10%FA	34	15
25%PC + 55%GGBS + 20%FA	41	17
25%PC + 65%GGBS + 10%LS	40	14
25%PC + 55%GGBS + 20%LS	48	21
25%PC + 40%GGBS + 35%LS	55	24
0.5 w/c ratio		
CEM I	10	10
65%PC + 35%GGBS	9	9
65%PC + 25%GGBS + 10%FA	12	12
65%PC + 25%GGBS + 10%LS	14	14
45%PC + 55% GGBS	14	14
45%PC + 45%GGBS + 10%FA	20	20
45%PC + 35%GGBS + 20%FA	24	24
45%PC + 45%GGBS + 10%LS	23	23
45%PC + 35%GGBS + 20%LS	30	30
25%PC + 75%GGBS	25	25
25%PC + 65%GGBS + 10%FA	34	34
25%PC + 55%GGBS + 20%FA	41	41
25%PC + 65%GGBS + 10%LS	40	40
25%PC + 55%GGBS + 20%LS	48	48
25%PC + 40%GGBS + 35%LS	55	55
0.65 w/c ratio		
CEM I	28	19
65%PC + 35%GGBS	25	16
65%PC + 25%GGBS + 10%FA	38	18
65%PC + 25%GGBS + 10%LS	34	18
45%PC + 55% GGBS	32	17
45%PC + 45%GGBS + 10%FA	52	22
45%PC + 35%GGBS + 20%FA	63	24
45%PC + 45%GGBS + 10%LS	47	22
45%PC + 35%GGBS + 20%LS	57	27
25%PC + 75%GGBS	52	25
25%PC + 65%GGBS + 10%FA	73	29
25%PC + 55%GGBS + 20%FA	88	32
25%PC + 65%GGBS + 10%LS	68	29
25%PC + 55%GGBS + 20%LS	80	41
25%PC + 40%GGBS + 35%LS	85	48

APPENDIX F: (CHAPTER 8) SUPPLEMENTARY INFORMATION

F-1 Carbonation

F-2 Chloride Ingress

F-1: Carbonation

Mix Combination	Depth of Carbonation, mm					
	0.35		0.5		0.65	
	5wks	20wks	5wks	20wks	5wks	20wks
CEM I	2	5	5	10	13	19
65%PC + 35%GGBS	4	6	7	11	12.5	18
65%PC + 25%GGBS + 10%FA	5	9	11	18	19	30
65%PC + 25%GGBS + 10%LS	4	8	8	13	14	22
45%PC + 55% GGBS	5	5.8	8	13	14.5	21
45%PC + 45%GGBS + 10%FA	6	12.5	13	22	22	34
45%PC + 35%GGBS + 20%PFA	9	16	16	26	25	38
45%PC + 45%GGBS + 10%LS	7	9	10	18	17	29
45%PC + 35%GGBS + 20%LS	8	10.5	13	19.5	19	32
25%PC + 75%GGBS	8	11	12	16	19	24
25%PC + 65%GGBS + 10%PFA	10	20	18	30	29	42
25%PC + 65%GGBS + 20%PFA	12.5	25	22	36	34	50
25%PC + 55%GGBS + 20%LS	13.5	18	18	26	29	42
25%PC + 40%GGBS + 35%LS	18.5	26	24	36	35	50

F-2: Chloride Ingress

Nix Combination	W/C Ratio	NON-STEADY STATERAPID CHLORIDE MIGRATION, NT BUILD-492 Dnssm, x10^{-12}m^2/s			RAPID CHLORIDE PERMEABILITY, ASTM CHARGE PASSED, COLOUMBS		
		28	90	180	28	90	180
CEM I	0.35	23.95	21.04	15.70	4181	3574	2935
CEM I	0.50	34.12	29.52	23.86	5195	4635	3655
CEM I	0.65	50.07	43.97	37.90	6905	6335	5200
65%PC + 35%GGBS	0.35	12.95	11.91	11.12	1800	1185	945
65%PC + 35%GGBS	0.50	15.80	14.22	13.23	2465	1775	1500
65%PC + 35%GGBS	0.65	21.65	19.00	17.45	3445	2825	2465
65%PC + 25%GGBS + 10%LS	0.50	8.41	4.29	4.33	2085	1690	1435
45%PC + 55% GGBS	0.35	11.60	10.41	9.55	1425	800	525
45%PC + 55% GGBS	0.50	14.20	12.68	11.62	2045	1322	1030
45%PC + 55% GGBS	0.65	19.10	17.03	15.15	3005	2100	1720
45%PC + 45%GGBS + 10%LS	0.35	3.81	2.59	1.65	1275	885	680
45%PC + 45%GGBS + 10%LS	0.50	6.56	4.47	2.99	1878	1474	1205
45%PC + 45%GGBS + 10%LS	0.65	12.76	9.05	6.99	2685	2015	1655
25%PC + 75%GGBS	0.35	10.21	9.22	8.60	1130	650	425
25%PC + 75%GGBS	0.50	12.21	10.81	10.02	1665	1140	850
25%PC + 75%GGBS	0.65	16.00	14.08	12.96	2555	1870	1550
25%PC + 40%GGBS + 35%LS	0.50	5.65	3.62	2.32	1605	1195	935
25%PC + 40%GGBS + 35%LS	0.50	9.65	8.11	7.03	2080	1640	1345